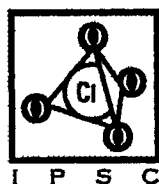




# Inter-Agency Perchlorate Steering Committee Stakeholder Forum

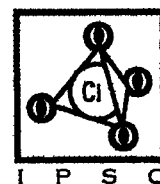


## Overview and History

25-27 August, 1998

Salt Lake City, UT

Phoenix, AZ

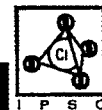


INFORMATIONAL BRIEFING

Lieutenant Colonel Dan Rogers, AFMC LO/JAV

## Overview

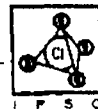
- Purpose
- Historical Information and Events
- IPSC Composition and Focus
- Forum Composition and Focus
- Where we are and Where we are going



## Purpose of the Forum

- Gather together the leading experts currently working on the perchlorate issue
- Provide the public with real-time information on perchlorate projects
- Listen to public concerns

*Inter-Agency Perchlorate Steering Committee*

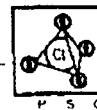


## Historical Events and Chronology

(before October 1996, I couldn't spell perchlorate)

- What is Perchlorate?
- Initial Objective!
- 27 Oct 96 Cleanup and Abatement Order
- Method Detection Capability
- TERA Peer Review
- State Regulatory Partnering
- 20/21 May - Protocol Meeting and Funding
- Inter Agency Perchlorate Steering Committee

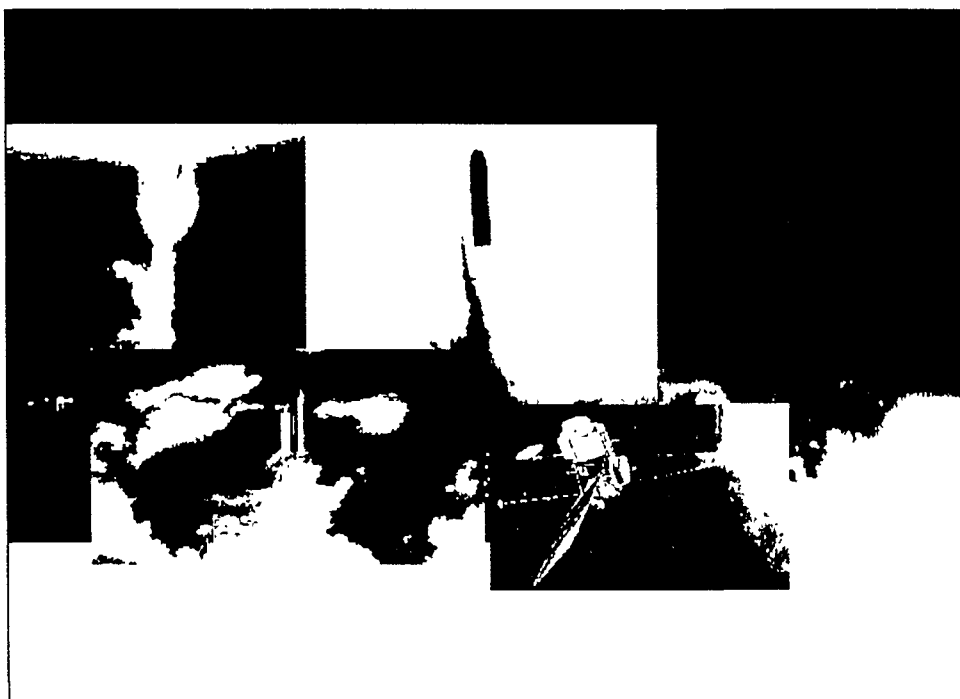
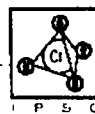
*Inter-Agency Perchlorate Steering Committee*



# What is Perchlorate?

- **Primary Oxidizer in Solid Rockets**
  - Titan, Minuteman, Peacekeeper, Hawk, Polaris, Space Shuttle
  - Army, Navy, Air Force, NASA
- **Neither Sinker Nor Floater**
- **Very Stable in Water**

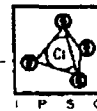
*Inter-Agency Perchlorate Steering Committee*



## Initial Objectives

- Evaluate and Understand Potential Health Risks Associated with Perchlorate in the Environment
- To Get the Best Scientific Information on the Toxicology of Perchlorate for Use by the Decision Makers and Most Importantly to the Public
- Partner with All Stakeholders
  - DoD, Industry, Research & Regulatory Community

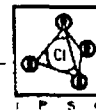
*Inter-Agency Perchlorate Steering Committee*



## Integrated Approach

- Analytical
- Health Effects
- Treatment Technology
- Ecological

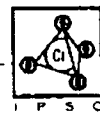
*Inter-Agency Perchlorate Steering Committee*



**October 96**  
**Central Valley Regional Water Quality  
Board**

- Cleanup and Abatement Order
- Emphasis on Observation of Plume Movement and Detection (MDL 400 ppb)
- Time-line for Cleanup of Groundwater
- Treatment Technology
  - Aerobic Pilot Project
  - Tyndall CRADA

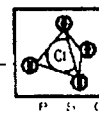
*Inter-Agency Perchlorate Steering Committee*



**Analytical Method Detection Limit  
(or how low can you go??)**

- Pre Jan 97.....400 ppb (Aerojet)
- January 97 .....100 ppb (Aerojet)
- April 97 ..... 4 ppb (DHS)
  - now replicated by CVRWQB, Aerojet and others
- Validation on both Aerojet and DHS Protocols by AF is Complete
- 1992/5 EPA “proposed” guidance level (4-18 ppb) based on provisional RfD

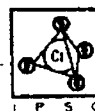
*Inter-Agency Perchlorate Steering Committee*



## March 97 Peer Review

- Convened by TERA, Sponsored by PSG
- Overall Recommendations
  - Data insufficient
  - Solid base of studies needed
  - Minimum studies recommended
  - AF expertise recognized
- Only “known” groundwater contamination site  
Sacramento

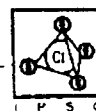
*Inter-Agency Perchlorate Steering Committee*



## Post Peer Review Activities

- Seek study funding
- Establish protocol review process
- Texpert team integration (Who?)
  - Internal (DoD)
  - External (PSG, State and Federal Researchers and Regulators)
- New source sites identified

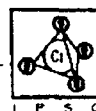
*Inter-Agency Perchlorate Steering Committee*



## Initial State Regulatory Partnering 21 April 97 Meeting

- Management level action officers and technical support staff
  - California DHS, DTSC, CVRWQB, OHEHA, PSG
- Partnership to serve the public
- Best value for taxpayer dollars
- Set meeting to decide best studies and protocol development

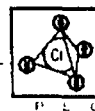
*Inter-Agency Perchlorate Steering Committee*



## May 1997 Perchlorate Protocol Review Meeting

- 20/21 May 1997 - Cincinnati
- Expert
  - USAF (AL/HSC/BCA), PSG, DHS, DTSC, OEIHA, EPA Superfund Office, NCEA, Ohio State, U of Cincinnati, Cytec Industries
- Goal?
  - Prioritized List of Reasonable Studies
  - Information Exchange
- California Still the Only "Site"

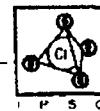
*Inter-Agency Perchlorate Steering Committee*



## Results

- Prioritized list of studies
- Promise to assist in protocol development
- Focus on the goal without regard to cost
- Share final protocol information with the public
- Begin studies as soon as possible
- Partnering to secure needed funding

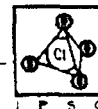
*Inter-Agency Perchlorate Steering Committee*



## Inter Agency Perchlorate Steering Committee (13 Jan 98)

- Purpose
- Sub Committees to address critical areas
- Membership
  - Federal and State Governmental Agencies
  - Tribal Representatives
- Meetings Open to Public
- Coordinate with AWWA-RF
- Public Stakeholder Forum

*Inter-Agency Perchlorate Steering Committee*



## **Inter-Agency Perchlorate Steering Committee -as of 21 May 1998-**

### **Executive Committee**

Peter Grevatt (EPA-OSWER)  
Kevin Mayer (EPA-IX)  
Lt Col Dan Rogers (DoD-USAF)  
Annie Jarabek (EPA-NCEA)  
Mike Osinski (EPA-OW)

### **Ecological Impacts (T/T)**

Mark Sprenger (EPA-OERR)  
Cornell Long (DoD-USAF)

### **Health Effects/Toxicity**

Dave Mattie (DoD-USAF)  
Annie Jarabek (EPA-NCEA)

### **Analytical**

Captain Dave Tsui (DoD-USAF)  
Steve Pia (EPA-NERL)  
Howard Okamoto (Cal-DHS)  
Sanwat Chaudhuri (Utah DEQ)

### **Treatment Technology**

Ed Urbansky (EPA-NRMRL)  
Wayne Praskins (EPA-IX)  
Jim Hurley (DoD-USAF)

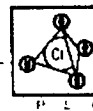
### **Peer Review**

Peter Grevatt (EPA-OSWER)

## **Forum Composition and Focus**

- Bring together the experts in health effects/toxicology, ecological impacts/transport and transformation, analytical methods and treatment technology
- Occurrence information
- Provide information on current initiatives
- Hear public and stakeholder concerns

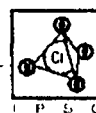
*Inter-Agency Perchlorate Steering Committee*



## Where We Are Today?

- Funded toxicology initiatives underway
- Funded treatment initiatives underway
  - AWWA-RF
  - Air Force, Army, NASA
- Partnership initiatives strong
  - Liaison with States of California, Nevada and Utah, Tribal Representation
  - Expect EPA revised RfD end Sept 98 with an external peer review in Oct 98

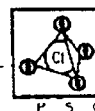
*Inter-Agency Perchlorate Steering Committee*



## Is There a Bottom Line?

- Goal - best scientific information to ensure protection of the nation's drinking water supply
- To get the best scientific information on the toxicology and occurrence of perchlorate to the decision makers and most importantly to the public
- Maintain an integrated approach
- Develop methods and technology as required

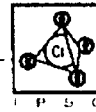
*Inter-Agency Perchlorate Steering Committee*



## Bottom Line (continued)

- There are no limits to the success of this innovative project because of its talented and dedicated team (They don't really care who gets the credit!)

*Inter-Agency Perchlorate Steering Committee*

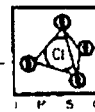


## Lt Col Dan Rogers

AFMC LO/JAV  
Environmental Law Directorate  
4225 Logistics Ave, Ste 23  
Wright Patterson AFB, Ohio 45433  
937-257-7287  
937-257-0537 (fax)  
drogers@jag.af.mil



*Inter-Agency Perchlorate Steering Committee*



## PERCHLORATE OCCURRENCE

Kevin Mayer  
Superfund Program  
U.S. EPA, Region 9



(415) 744-2248

mayer.kevin @epamail epa.gov

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## PERCHLORATE OCCURRENCE



- History - Before 1997
- Perchlorate Users
  - Facilities
  - Locations
- Perchlorate in the Environment
  - Occurrence Nationwide
  - California Wells
  - Nevada

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## HISTORY - Before 1997

- 1980s - Aware of Perchlorate in CA, NV
- 1985-86 - San Gabriel Valley
- 1990s - Rancho Cordova (ppm)
- 1992-95 - Provisional Reference Dose (ppb range)
- 1997 - Analytical breakthrough



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## San Gabriel Valley Superfund Site



- Large, complex groundwater site
- Perchlorate suspected
- Colorimetric test (0.02-0.05 mg/l) in 1985
- Preliminary data positive
- Toxicological request in Dec. 1985

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## San Gabriel Valley Superfund Site



- Quality Assurance Problems
  - Sample blanks - False positives
  - Cannot Validate Data
- All Perchlorate Results Rejected
- ATSDR: Better Analysis First
- No Immediate Developments in Analysis

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### Agency for Toxic Substances and Disease Registry - ATSDR (January 21, 1986):

" Given the proprietary nature of the laboratory method for quantification and the poor quality assurance results noted, the **data do not prove that perchlorate ion has actually been found** if the presence of perchlorate ion is confirmed the **scientific database** on this ion is **insufficient to generate either an acute or longer-term health advisory for drinking water**"

" The minimal acute toxicity data available suggest that one or two ppm perchlorate ion would not represent an immediately acute and substantial threat to the public health. The ATSDR does not consider this level to be "safe" in the absence of experimental data "

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## **Aerojet General Superfund Site (Rancho Cordova)**



- Perchlorate > 1 mg/l in groundwater
  - Detectable by EPA method (Ion Chromatography)
- Region 9 requests Provisional RfD from NCEA EPA Nat'l Center for Environmental Assessment
- December, 1992: 4 micrograms/liter (ppb)
- October, 1995 range: 4-18 ppb
- Analytical Limit 400 ppb

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## **USES of PERCHLORATE**

- 90% Solid Rocket Fuel Oxidizer
- Explosives
- Fireworks and Pyrotechnics
- Reported in Nitrate Fertilizer from Chile



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## **PERCHLORATE SHIPMENTS**



- Manufacturer's Information
- About 150 facilities
- 35+ States
- Most Information in Last 20 Years

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## PERCHLORATE in the ENVIRONMENT



- UTAH, ARKANSAS, NEW YORK wells, also MARYLAND, TEXAS
- American Water Service Survey
  - 425 wells, 7 hits (4 states)
- CALIFORNIA
  - Over 500 Water Supply Wells Tested
  - About 110 Reported, More than 30 Wells over 18 ppb

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## EXAMPLE FACILITIES



- Many Rocket Manufacturing/Testing
  - Aerojet, Lockheed, JPL
- Whittaker - Ordinance and Missiles
- Rialto - Ammunition, Fireworks and Rockets
- LLNL Site 300 - Explosives (Alpha Explosives, Lincoln CA )

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## COLORADO RIVER and LAKE MEAD



- Southern California Aqueduct
- Lake Havasu (Colorado River)
- Lake Mead
- Non-Detect Upstream
- Downstream of Parker Dam

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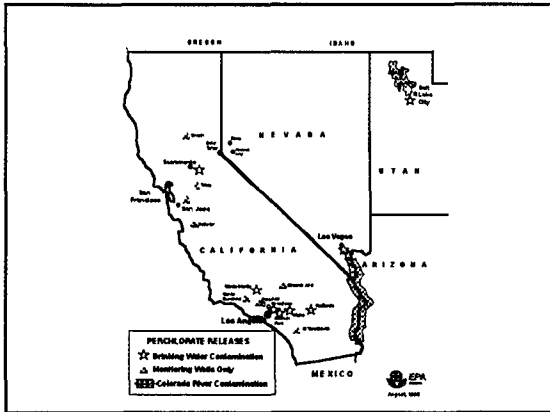
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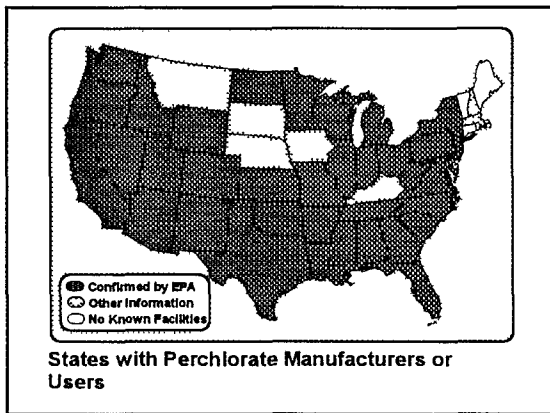
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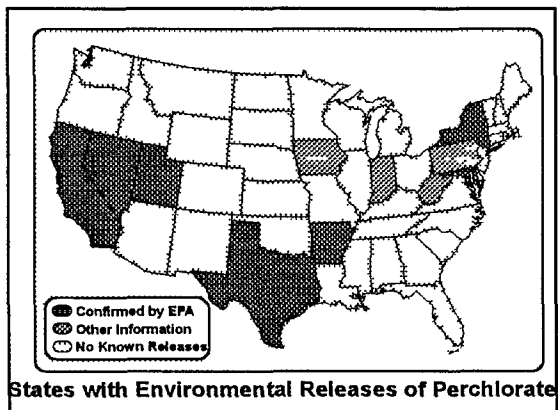
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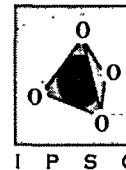
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## **Testing Strategy and the Revised RfD / Risk Assessment**

**Annie M. Jarabek**  
**National Center for Environmental Assessment**  
**U.S. Environmental Protection Agency**



**Perchlorate Stakeholders Forums**  
**Sponsored by the IPSC**  
**Salt Lake City, UT and Phoenix, AZ**  
**August 25 and August 27, 1998**



## **The Perchlorate Contamination Challenge Credible Science**



## **Credible Decisions**

- **Accurate risk characterization**
- **Appropriate management strategies**

## **The Perchlorate Contamination Challenge**

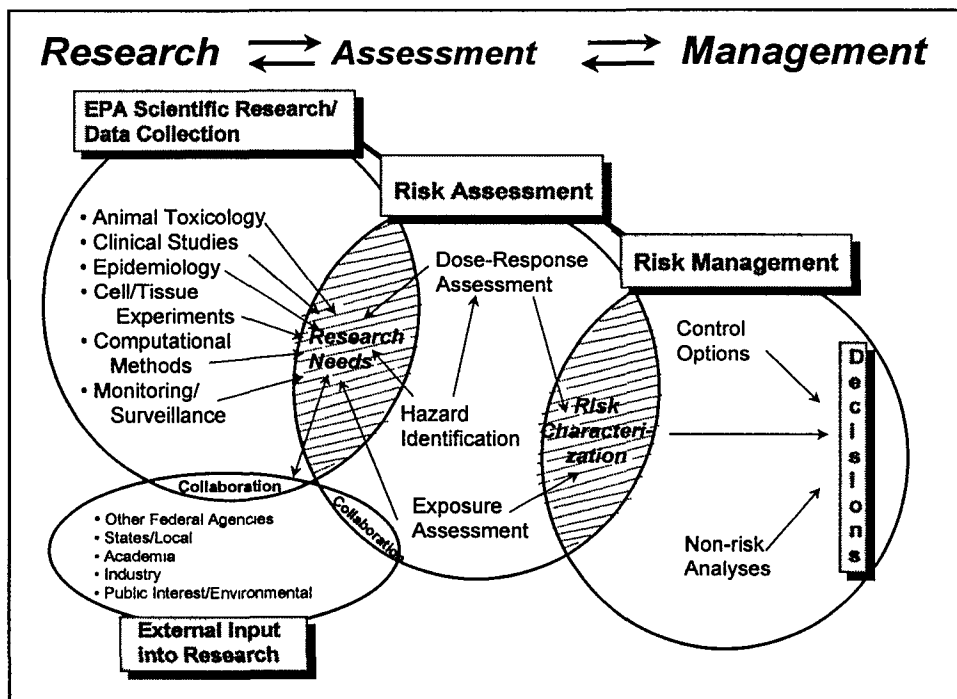
### **An Integrated Approach**

- Occurrence survey
- Stakeholder issues
- Health effects / toxicology
- Analytical methods (detection limit)
- Ecological impact / transport and transformation
- Treatment technology
- Technology transfer

## **The Perchlorate Contamination Challenge**

### **Pro-Active Partnership**

- Unprecedented timeframe
- Targeted expertise



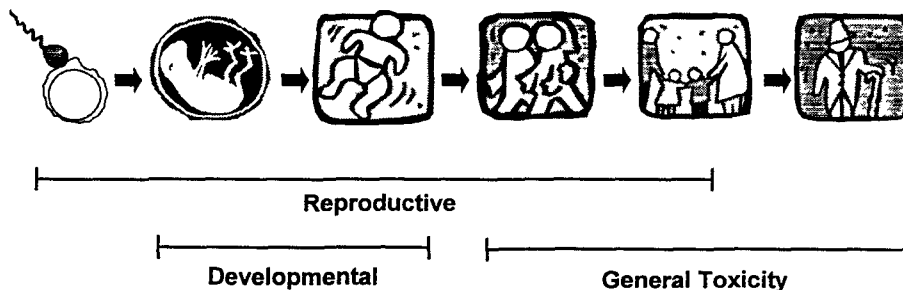
## Outline

- **Background**
  - Definition of the RfD
  - Derivation of the RfD
  - Basis of the provisional RfD
- **Review of perchlorate database**
- **Recommended new studies**
  - Description of different study designs
  - Objectives of each study
  - Strategy for synthesis of data
- **Summary**

## Definition

An oral reference dose (RfD) is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer health effects during a lifetime.

**A High Confidence RfD is Based on Data that Addresses All Potentially Critical Life Stages.**



## **Minimum Data Base for Derivation of an RfD**

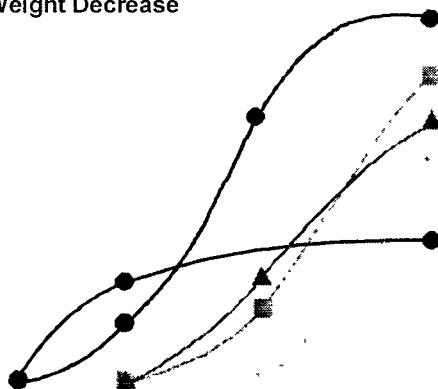
- \* Rationale is to address all potentially critical life stages
- \*\* Rationale is to use different species to evaluate variability in species sensitivity unless a particular laboratory animal model is more appropriate

## **RfD Derivation**

- Hazard identification and data array analysis
- Designation of effect levels (NOAEL, BMD)
- Choice of critical effect
- Dosimetric adjustment
- Application of uncertainty factors (UF)
- Characterization of uncertainty (confidence levels)

### Data Array and Oral Reference Dose (RfD) Derivation

- Indicator Enzyme
- Slight Body Weight Decrease
- 
- ▲



Indicator Enzyme

●

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$$RfD = \frac{NOAEL*[HED]}{UF \times MF}$$

Where:

**NOAEL\*[HED] =**

The NOAEL or equivalent effect level obtained with an alternate approach (\*), dosimetrically-adjusted to a human equivalent dose [HED].

**UF =**

Uncertainty factor(s) applied to account for the extrapolation required from the characteristics of the experimental regimen to the assumed human scenario, and

**MF =**

Modifying factor to account for scientific uncertainties in the study(ies) chosen as the basis for the operational derivation, e.g., poor statistical power or exposure characterization.

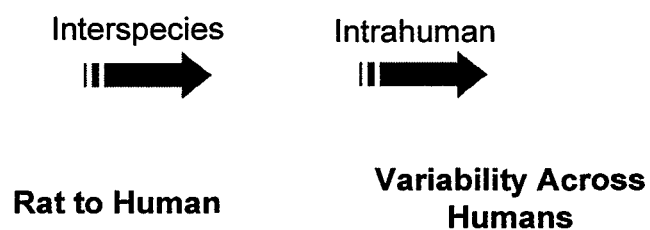
## Factors for Uncertainties in Applied Extrapolations

10 <sub>H</sub>	Human to Sensitive Human
10 <sub>A</sub>	Experimental Animal to Human
10 <sub>S</sub>	Subchronic to Chronic Duration
10 <sub>L</sub>	LOAEL(HEC) to NOAEL(HEC)
10 <sub>D</sub>	Incomplete to Complete Data Base

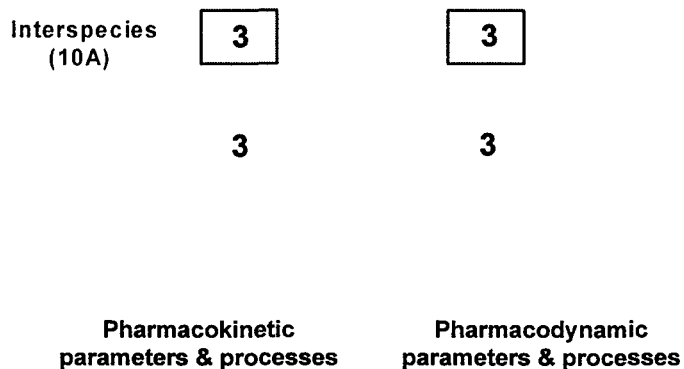
### Modifying Factor

**MF Professional Assessment of Scientific Uncertainties of the Study and Data Base not Explicitly Addressed Above. Default for the MF is 1.0 e.g., applied for small sample size or poor exposure characterization.**

## Extrapolation Uncertainties



## Schematic of UF Components Incorporated Into Exposure-Dose-Response Characterization



## **Basis of the Provisional RfD**

- Initial correspondence to EPA Region IX (Dec 92) from Superfund Health Risk Technical Support Center (NCEA-Cin)
- Principal study = Stanbury & Wyngaarden (1952)
- NOAEL = 0.14 mg/kg-day for 100% iodide release
- UF = 1000
  - intrahuman variability (10)
  - less than chronic data (10)
  - database deficiencies (10)
- Drinking water criteria = 3.5 ppb based on 70 kg / 2 L water

## **Second Provisional RfD (1995)**

- Revision based on PSG submission to Superfund Health Risk Technical Support Center (NCEA-Cin)
- Same principal study and NOAEL
- Different UF
  - intrahuman variability (10)
  - less than chronic data (10)
  - database deficiencies decreased (3)
- Drinking water criteria = 18 ppb based on 70 kg / 2 L water

**Provisional RfD  
March 1997  
External Peer Review**

- **Proposed by TERA**
- **Same principal study, critical effect**
- **Another, different UF = 100**
  - intrahuman reduced (3)
  - subchronic to chronic (3)
  - LOAEL to NOAEL (3)
  - Database deficiencies (3)

**March 1997  
External Peer Review**

- **Inadequate data base for RfD derivation**
- **Available mechanistic insights suggest special studies and synthesis strategy**
- **Eight (8) additional new categories of studies recommended**

## **Deficiencies of Clinical Data**

- **Adult subjects**
- **Typically subjects with thyroids altered by disease or other treatments**
- **Few pregnant subjects**
- **Acute or short-term exposure duration**
- **Limited range of doses**

## **Susceptibility**

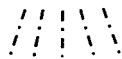
The potential for increased susceptibility is due to factors that influence:

- (1) **Exposure e.g., activity patterns and location**
- (2) **Deposition / uptake and the internal target tissue dose (i.e., pharmacokinetic parameters) and toxicant-target interactions, e.g., metabolism rates or pathways**
- (3) **Tissue sensitivity (pharmacodynamics) - conditions which alter or enhance target tissue response, e.g., age, nutritional status, or disease states**

## Outline

- **Background**
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  - Derivation of the RfD
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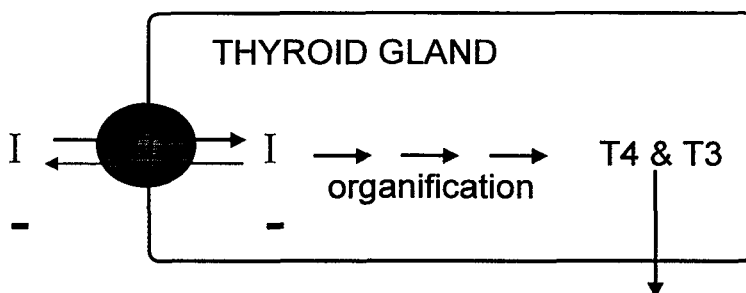
## Established Perchlorate Toxicity



The only systematically studied and established effect is the anti-thyroid effect due to competitive inhibition of iodine uptake.



## Iodine and the Thyroid Gland



National Health and Environmental Effects Laboratory



## Main Symptoms/Effects of Hypothyroidism

### Developmental

- delayed reflex ontogeny
- impaired fine motor skills
- deaf-mutism, spasticity
- gait disturbances
- mental retardation
- speech impairments

*transient disruption leads  
to permanent effects*

### Adult

- run down, slow, depressed,
- sluggish, cold, tired
- dryness and brittleness of hair
- dry and itchy skin, constipation
- muscle cramps
- increased menstrual flow

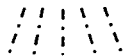
*transient disruption leads to  
transient effects*

\*thyroid tumors in rodents

National Health and Environmental Effects Laboratory



## Potential Perchlorate Toxicity

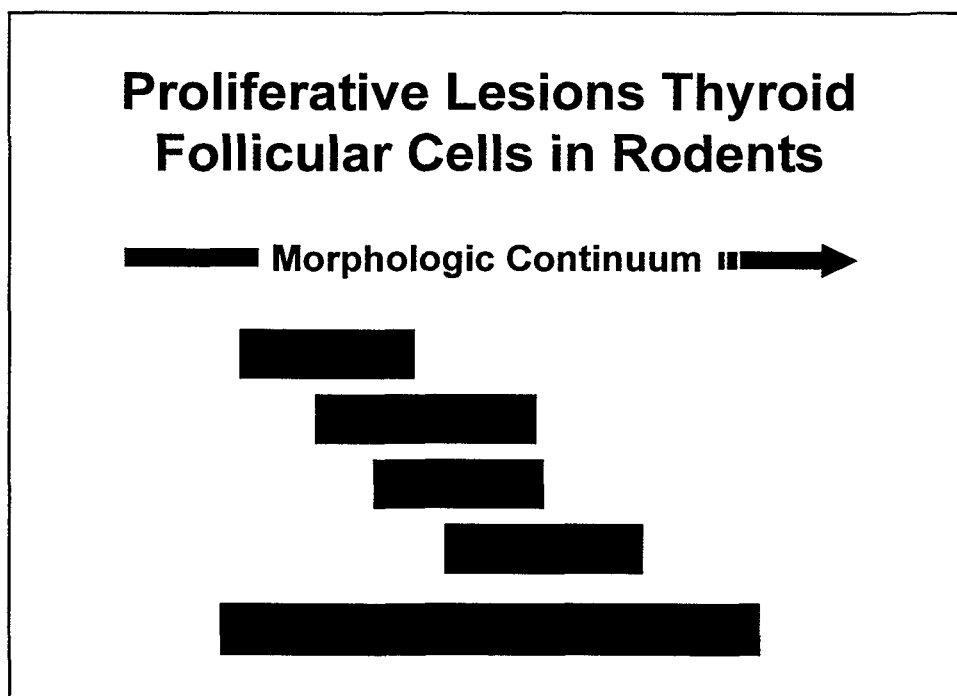
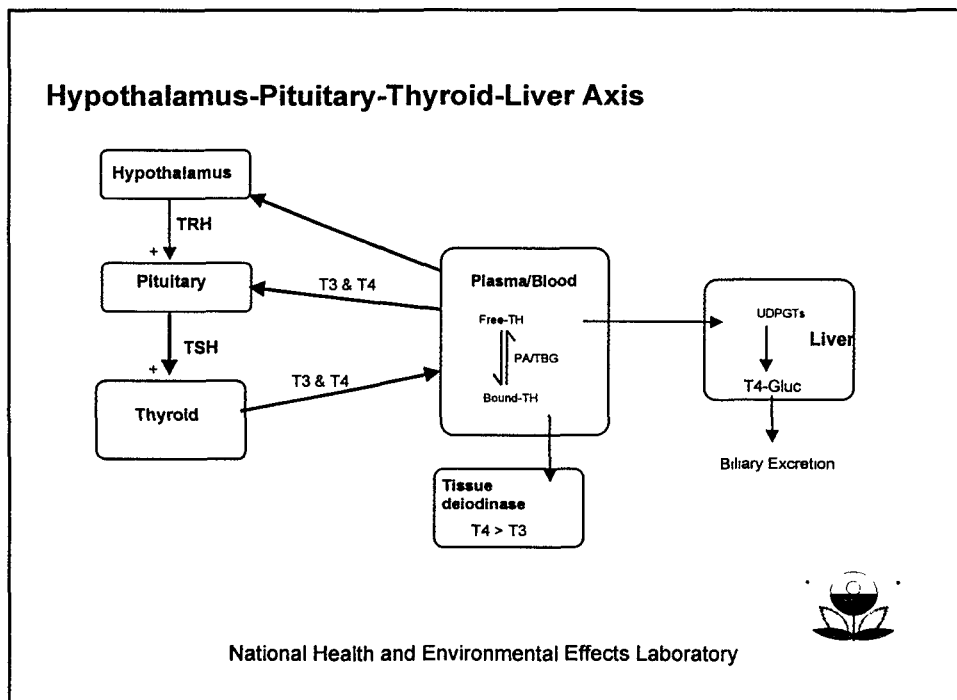


Anti-thyroid effect  
in pregnant women  
might cause  
adverse effect in  
developing fetus.



## Mechanisms of Anti-Thyroid Mediated Neoplasia in Rodents

- DNA Directed:
  - X - rays
  - <sup>131</sup>I
  - Genotoxic chemicals
- Indirect
  - Partial thyroidectomy
  - Transplantation of TSH-secreting pituitary tumors
  - Iodide deficiency
  - Chemicals inhibiting iodide uptake
  - Chemicals inhibiting thyroid peroxidase
  - Chemicals inhibiting TH
  - Chemicals inhibiting conversion of T3 & T4
  - Chemical inhibiting hepatic thyroid hormone metabolism and excretion



## **Mode of Action Provides Important Insight to Characterization of Toxicity**

- A chemical's influence on the molecular, cellular, and physiological functions in producing tumors
- Prolonged depression of TH causes a feedback that leads to upregulation of TSH which leads to thyroid gland hyperplasia
- Genotoxic?

## **Additional Suggested Target Tissues**

- Reproductive function
- Immune function
  - aplastic anemia
  - leukopenia

## **Existing Data Summary**

- Target tissue appears to be the thyroid but available testing not comprehensive across endpoints
- Anti-thyroid effects would differ among adult versus developing fetus, children
- Anti-thyroid effects associated with benign neoplasia development in rats; a nonlinear process
- Genotoxicity not characterized
- Relevancy to human risk of rat tumors not established; presumed protective

## **Outline**

- Background
  - Definition of the RfD
  - Derivation of the RfD
  - Basis of the provisional RfD
- Review of perchlorate database
- Recommended new studies
  - Description of different study designs
  - Objectives of each study
  - Strategy for synthesis of data
- Summary

## **Recommended Studies**

- 90-Day subchronic bioassay
- Developmental neurotoxicity study
- Genotoxicity assays
- Mechanistic studies
- ADME - Absorption, Distribution, Metabolism and Elimination
- Developmental study
- 2-Generation reproductive toxicity study
- Immunotoxicity

## **EPA Risk Assessment Guidelines**

- Principles and procedures to frame the conduct of risk assessments
- Promote consistency and technical quality of scientific inferences
- Flexible, full consideration to all relevant scientific information case-by-case
- Revised as experience and scientific consensus evolve

## **EPA Risk Assessment Guidelines**

- Developmental toxicity (1991)  
FR 56(234): 63798 - 63826
- Reproductive toxicity (1997)  
EPA No. EPA/630/R-96/009a  
NTIS PB97-100093
- Neurotoxicity (1998)  
EPA No. EPA/630/R-95/001Fa  
NTIS PB98-117831
- Thyroid follicular cell tumors (1998)  
EPA/630/R-97-002

## **EPA Perchlorate Toxicity Risk Assessment Team**

- |                    |        |  |
|--------------------|--------|--|
| • Harlal Choudhury | NCEA   | General toxicology / risk assessment             |
| • Eric Clegg       | NCEA   | Reproductive toxicology                          |
| • Kevin Crofton    | NHEERL | Neurotoxicology                                  |
| • Vicki Dellarco   | OW     | Genetic toxicology                               |
| • Annie Jarabek    | NCEA   | General toxicology / dosimetry / risk assessment |
| • Gary Kimmel      | NCEA   | Developmental toxicology                         |
| • Ralph Smialowicz | NHEERL | Immunotoxicology                                 |

## **Toxicity Study Review and Revised RfD / Risk Assessment**

- Review of existing and new toxicity data
- Hazard identification
- Dose-response evaluation
  - Designation of effect levels (mathematical modeling or NOAEL / LOAEL procedure)
  - UF assignment
  - Uncertainty characterization - confidence statements

## **90-Day Subchronic Bioassay**

- Tests for additional target tissues
- Minimum database for RfD derivation
- Added additional tests for:
  - reproductive parameters
  - mutagenic effects in bone marrow
  - thyroid hormone levels
- Objective is to ascertain if anti-thyroid effect is critical and its dose-response

### **Developmental Neurotoxicity Study in Rats**

- Examines potentially critical effect and population: evaluates nervous system (structure and function) of fetal, newborn, and young animals
- Added thyroid histopathology and thyroid hormone level determinations to characterize anti-thyroid effect in offspring

### **Genotoxicity Battery**

- Tests for toxicity to DNA in various assays
- Provides mode-of-action information to evaluate potential for carcinogenicity
- May impact consideration of uncertainty factor for less than chronic data

## **Immunotoxicity Study**

- Evaluates immune system structure and function
- Motivated by case reports of aplastic anemia and leukopenia
- May reduce UF for database deficiencies if not critical effect

## **Developmental Study in Rabbits**

- Endpoint required for greater confidence in database, may reduce UF for data deficiencies if not critical effect
- Definitive test for toxicity during organ development (birth defects)
- Added hormone analysis and thyroid histopathology to evaluate second species

## **2-Generation Reproductive Toxicity Study**

- Evaluates fertility of adults and viability of (toxicity in) offspring in rats
- Tests for reproductive parameters over two generations
- Added analysis of thyroid hormones and thyroid histopathology at various time points
- Endpoint required for greater confidence in database, may reduce UF for database deficiencies if not critical effect

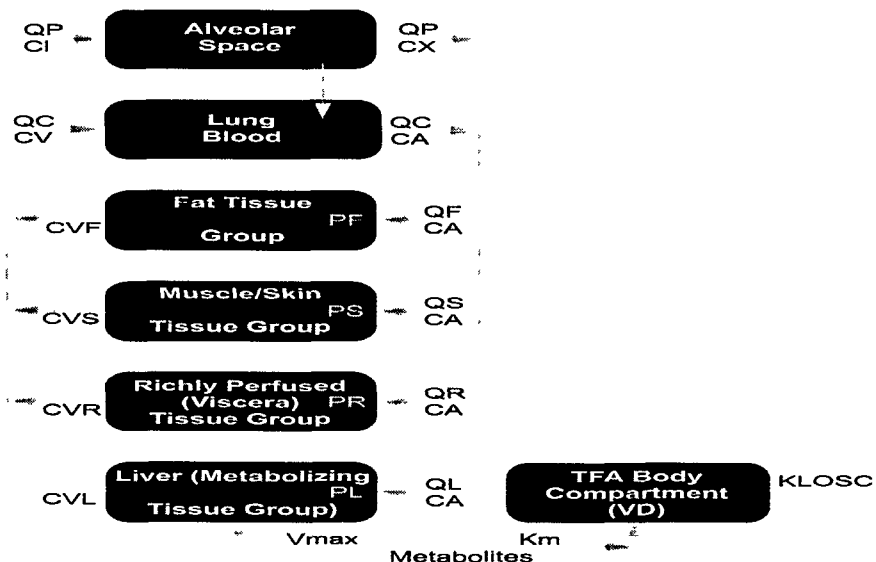
## **ADME study**

- Literature review of perchlorate discharge test
- Protocols proposed to evaluate perchlorate kinetics, iodine inhibition kinetics and thyroid hormone homeostasis
- Basis for development of physiologically-based pharmacokinetic (PBPK) model

## Mechanistic Studies

- Aid to quantitative interspecies extrapolation - basis to extend PBPK model
- Additional developmental studies to evaluate thyroid TH in fetal and post-natal periods
- Determine relative sensitivity of fetal/postnatal thyroid versus adult
- Determine relative sensitivity of rat versus human

## PBPK Model Schematic



## **Outline**

- **Background**
  - Definition of the RfD
  - Derivation of the RfD
  - Basis of the provisional RfD
- **Review of perchlorate database**
- **Recommended new studies**
  - Description of different study designs
  - Objectives of each study
  - Strategy for synthesis of data
- **Summary**

## **Greatest Assessment Difficulty: Designation of Adversity**

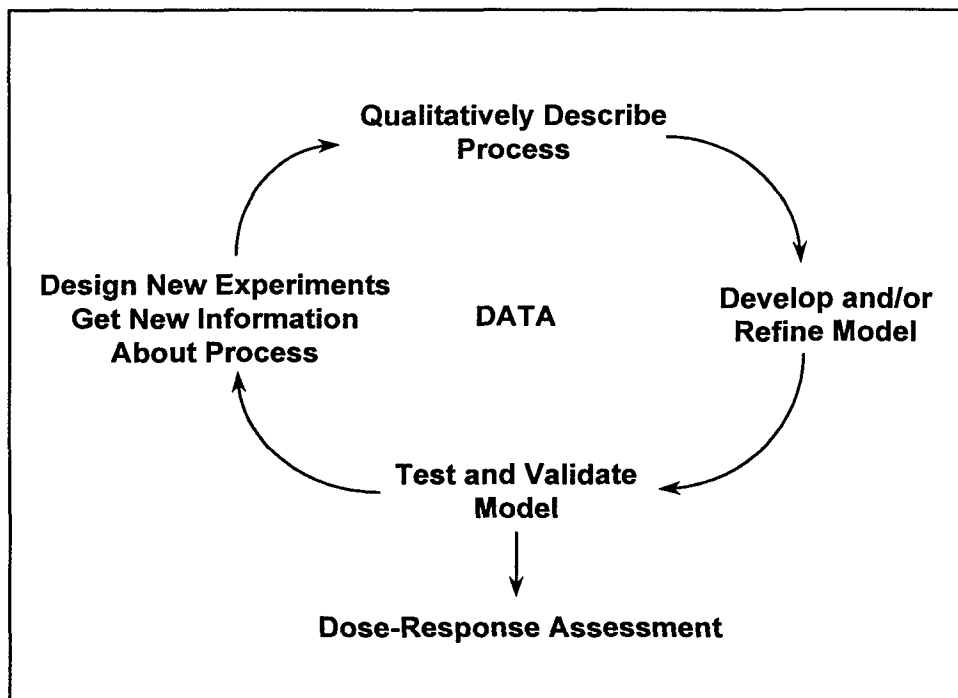
- Reversible effects in adults versus permanent deficits in developing fetus
- How can thyroid hormone data inform interpretation of adverse levels for both effects?

### **Revised RfD / Risk Assessment Review Process**

- Internal peer review (October 1998)
- External peer review (November 1998)
- Response / revisions subsequent to external peer review (December 1998)
- Submit final revised RfD / risk assessment to Integrated Risk Information System (IRIS) process
- Refine as required with new data

### **Revised RfD**

- Toxicity bioassay data across comprehensive array of endpoints to establish target tissue
- Mechanistically-motivated special studies to characterize critical dose-response relationships
- New occupational and epidemiology surveys
- Future refinements as required by new data



## **Annie M. Jarabek**



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## **Development, QA/QC and Status of Study Protocols**

**David R. Mattie, PhD, DABT  
Operational Toxicology Branch  
AFRL/HEST**

**Perchlorate Stakeholders Forum  
Sponsored by the IPSC  
Salt Lake City, UT and Phoenix, AZ  
August 25 and 27, 1998**



## **Required for All Recommended Studies**

- **Good Laboratory Practice Standards  
EPA (40 CFR Part 792)**
- **Animal Housing and Care Based on  
Association for Assessment and  
Accreditation of Laboratory Animal  
Care (AAALAC) and Guide for the Use  
of Laboratory Animals (NIH Publication  
No. 96-03, 1996)**



## Standard Operating Procedures

- Protocol review by expert panel
- EPA guideline testing requirements
- Standardized QA/QC process



## QA/QC Procedures Air Force Sponsored Studies

- Contract lab delivers draft report to AFRL for review by contract monitor and project director
- Review includes:
  - QA/QC to confirm study conducted according to protocol requirements
  - Contractual review for form and contract requirements



### **QA/QC Procedures Air Force Sponsored Studies**

- **Comments returned to contract lab**
  - **Editorial, contractual, format**
- **Contract lab addresses comments**
- **Final draft to AFRL for technical review by Senior Scientist and associates with necessary expertise**
- **Contractor addresses final comments**
- **Final report delivered to AFRL**
- **AFRL sends to EPA/NCEA within 48 hours**



### **QA/QC Procedures PSG Sponsored Studies**

- **Contract lab delivers draft report to TERA/PSG for review by contract monitor**
- **Review includes:**
  - **QA/QC to confirm study conducted according to protocol requirements**
  - **Contractual review for form and contract requirements**
  - **Editorial, contractual, format**



### QA/QC Procedures PSG Sponsored Studies

- **Draft report undergoes technical review by AFRL Senior scientist and associates with necessary expertise**
- **Contractor addresses all comments**
- **Final report delivered to TERA/PSG**
- **TERA/PSG sends to EPA/NCEA within 48 hours**



### QA/QC Procedures Summary

- **Standardized review process for all studies**
- **Technical review by AF Senior Scientist team**
- **Commitment to expedited review process to accommodate assessment schedule**



### Report Status

- **Completed Final Reports available for EPA/NCEA assessment:**
  - 90-Day bioassay (5/98)
  - Developmental neurotoxicity study (6/98)
  - Genotoxicity battery (7/98)
  - Developmental study (9/98)



### Report Status

- **Completed Interim reports available for EPA/NCEA assessment:**
  - ADME / Mechanistic (9/98 through 5/99). Final PBPK model due 9/99.
  - 2-Generation reproductive (9/1/98: PO and F1 generation; F2 and Final report 2/98)
  - 8. Immunotoxicity (14-, 90-, and 120-day assays on 8/3/98; host resistance and tumor models 11/98)

8/25/98 SLC, UT and 8/27/98 PHX, AZ Stakeholder Forums: D.R. Mattie



**David R. Mattie PhD, DABT**  
**Director of R&D Business Development**  
**Operational Toxicology Branch**  
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## ***Peer Review of Perchlorate Risk Assessment***

Peter Grevatt, Ph.D., U.S. EPA HQ

### **Presentation Goals**

- Define Peer Review
- EPA Peer Review Policy
- Purpose of Peer Review
- Scope of Peer Review for Perchlorate
- Impact on Perchlorate Risk Assessment

### **Define Peer Review**

- *"Documented critical review of Agency scientific or technical work product"*
  - In-depth Assessment
  - Conducted by qualified individuals
  - Independent of those who performed work
  - Equivalent in technical expertise

## EPA Peer Review Policy

- *"Major scientifically and technically based work products related to Agency decisions should be peer reviewed..."*
- *"For those work products that are intended to support the most important decisions or that have special importance in their own right, external peer review is the procedure of choice..."*

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## Purpose of Peer Review

- Ensure quality, credible Agency decisions
- Preparation of sound, technically defensible analyses and work products.

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## Scope of Perchlorate Peer Review

- Independent, external peer review of all aspects of the perchlorate risk assessment
- EPA Office of Solid Waste and Emergency Response will oversee peer review
  - Study protocols
  - Study results
  - Development of reference dose
    - Selection of critical endpoint
    - Use of uncertainty factors
  - Risk characterization

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### Scope of Perchlorate Peer Review

- Stakeholder participation
  - Nomination of expert peer reviewers
    - Selection by independent scientific panel
    - Examination of potential conflict of interest
  - Open peer review panel meeting
  - Opportunity for comment by interested parties
  - Preparation of final peer review report

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### Impact on Perchlorate Risk Assessment

- Submit Final Peer Review Report to NCEA
- Preparation of Responsiveness Summary
  - Detailed response to all peer review comments
    - Comments addressed
    - Explanation of Changes
- Completion of final risk assessment

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### Where to reach me!

**Peter Grevatt Ph.D.**  
Acting Science Advisor  
U.S. EPA HQ  
Office of Solid Waste and Emergency Response  
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401 M St., S.W.  
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202-260-3100, 202-401-1496 (fax)  
grevatt.peter@epa.gov

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## The Safe Drinking Water Act and Perchlorate

MIKE OSINSKI  
Office of Ground Water and Drinking Water  
U.S. Environmental Protection Agency  
Washington, D.C.

202-260-6252 202-260-3762 (fax)  
OSINSKI.MICHAEL@epamail.epa.gov

### Contaminant Identification and Selection Under the SDWA

- **Contaminant Selection Under the 1986 Amendments to SDWA:**
  - ⇒ Regulate 83 contaminants by 1989;
  - ⇒ Regulate 25 contaminants every 3 years.
- **Congress, EPA had Implementation Concerns:**
  - ⇒ Missed statutory deadlines;
  - ⇒ Water systems encountered difficulty in timely compliance;
  - ⇒ Focus on sound science and contaminants posing greatest risk.

### Contaminant Identification and Selection Under the SDWA

- **Contaminant Selection Under the 1996 Amendments to SDWA.**
  - ⇒ Publish a Contaminant Candidate List (CCL) of contaminants known or anticipated to occur in DW and not subject to NPDWRs by Feb 1998.
  - ⇒ Broad consultation with stakeholders, NDWAC, and SAB.

### Contaminant Identification and Selection under the SDWA

- **Draft CCL Published on Oct 6, 1997.**
  - ⇒ Did not include perchlorate, but sought comment on whether to include it on the final CCL.
  - ⇒ Public comments indicated overall support for adding perchlorate to the CCL.
- **Final CCL published on March 2, 1998.**
  - ⇒ Contains 50 chemical and 10 microbiological contaminants.

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### Contaminant Candidate List (CCL)

- **Functions of the CCL:**
  - ⇒ Make determinations for at least 5 contaminants of whether or not to regulate with a NPDWR by 2001.
  - ⇒ Focus and prioritize research agenda for contaminants with data gaps.
  - ⇒ Source for selection of contaminants for unregulated contaminant monitoring regulation (UCMR) due in 1999.

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### Perchlorate and the CCL

- **Two categories of contaminants on the CCL:**
  - ⇒ (1) Regulatory Determination Priorities;
  - ⇒ (2) Research Priorities.
- **Perchlorate falls into the research priorities category due to extensive data gaps in:**
  - ⇒ Occurrence; health effects, treatment technologies, and analytical methods research.

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### Regulatory and Policy Agenda for Perchlorate

- **Determination to regulate not likely by 2001.**
  - ⇒ Extensive data gaps in all areas
- **EPA is not currently planning to include perchlorate as a contaminant in the proposed UCMR (Fall 1998).**
  - ⇒ Lack of EPA approved analytical method(s)
  - ⇒ Recommend near-term special occurrence studies

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### Next Steps for Perchlorate

- **Perchlorate is a research and occurrence priority for the OGWDW.**
  - ⇒ In process of developing short and longer term research plans on health, treatment, and analytical methods
- **OGWDW is very engaged in the IPSC.**
  - ⇒ Ensure exchange of scientific information to support decision making based on sound science and stakeholder involvement

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### Next Steps for Perchlorate

- **Possible Scenarios:**
  - (1) **Longer Term (3 to 5 years):**
    - ⇒ Data gaps filled and perchlorate moves to the regulatory determination priority category of next CCL – due in 2003
  - (2) **Near Term (1-2 years):**
    - ⇒ If health effects and occurrence data warrant, develop a Health Advisory

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### EPA Health Advisory Program

■ **SDWA General Authority:**

⇒ "The Administrator may publish health advisories (HA), which are not regulations, or take other appropriate actions for contaminants not subject to any national primary drinking water regulation."

- **HAs represent concentrations of contaminant in drinking water which adverse health effects are not expected to occur.**

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### EPA Health Advisory Program

- **Not federally enforceable.**

- **Subject to change as new information becomes available.**

- **Can serve as technical guidance to assist State, Tribal, and local officials responsible for protection of public health.**

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### EPA Health Advisory Program

- **HAs used in emergency situations and describe concentrations of a contaminant at which adverse non-carcinogenic effects are not anticipated to occur following exposures:**

- 1-day
- 10-day :
- Longer term (i.e. 7 years)
- Lifetime

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### Sample HA Calculations

- Determine RfD in mg/kg/day.
- Determine DWEL (Drinking Water Equivalent Level) in mg/L, assuming 100% drinking water contribution.
- Determine HA in mg/L.

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### Sample HA Calculations

- $DWEL (mg/L) = \frac{(RfD)(70 \text{ kg adult})^*}{(2 \text{ L/day})}$
- $DWEL (mg/L) = \frac{(RfD)(10 \text{ kg child})^{**}}{(1 \text{ L/day})}$
- \* for lifetime HA
- \*\* for 1 day, 10 day, and longer term HA
- $HA (mg/L) = (DWEL)(\% \text{ DW contribution})$

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David T. Tsui, Capt., USAF

Air Force Research Laboratory  
Toxicology Branch  
Wright-Patterson AFB, OH

Sanwat Chaudhuri, Ph. D.  
Steve Dickson

Utah Department of Health

8/25/98

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IPSC

Analytical Chemistry Method Sub-Committee

- ◆ Sanwat Chaudhuri, UDOH
- ◆ Howard Okamoto, CDHS
- ◆ Steve Pia, USEPA-NERL
- ◆ David Tsui, AFRL/HEST

2

## Topics

- ◆ Perchlorate Analysis
  - ◆ Chemistry of Perchlorate
  - ◆ Analytical Techniques
  - ◆ Ion Chromatography (IC)
- ◆ Method Parameter Studies
- ◆ Stability Study
- ◆ Inter-laboratory Study on the Performance of IC Methods
- ◆ Anion Interference Study - AS-11

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## Chemistry of Perchlorate

- ◆ Oxidation: + 7
- ◆ Structure:  $sp^3$ ,  $T_d$
- ◆  $ClO_4^-$  is a Very Weak Base of  $HClO_4$
- ◆  $HClO_4$  is a Very Strong Acid
  - ◆ Thermodynamically and Kinetically Unstable
- ◆  $ClO_4^-$  is a "Polarizable" Anion
  - ◆ Low Hydration Energy
  - ◆ Small Hydrated Radius (hydrophobic)
  - ◆ Strong Interactions with  $\pi$  Electrons
- ◆ Perchlorate Salts are Soluble in Water

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## Solubility of Perchlorate Salts

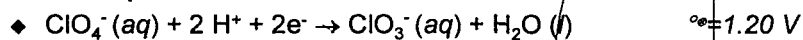
◆	Mol Wt.	Cold (g/L)	Hot (g/L)
◆ Ammonium	101.49	2.87	11.5
◆ Sodium	122.44	s.	v.s.
◆ Potassium	138.55	0.075	2.18
◆ Magnesium	223.21	9.93	v.s.
◆ Calcium	238.98	18.86	v.s.
◆ Aluminum	433.43	s.	s.
◆ Nickel	365.68	22.25	27.37
◆ Lead	460.15	49.97	n.a.
◆ Iron	254.75	v.s.	n.a.

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## Thermodynamics of Redox Rxns

### ◆ Thermodynamically favorable

#### ◆ At pH = 0:



#### ◆ At pH = 14:



#### ◆ Highly energetic at extreme pH's

#### ◆ Powerful oxidant at extreme pH's

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## Kinetics of Redox Rxns

- ◆ Kinetically Unfavorable
- ◆ Rule of Thumb: Rate of Oxidation Increases as the Oxidation Number of the Halogen Decreases
- ◆  $\text{ClO}_4^- < \text{ClO}_3^- < \text{ClO}_2^- \ll \text{ClO}^- \sim \text{Cl}_2$
- ◆  $\text{BrO}_4^- < \text{BrO}_3^- \ll \text{BrO}^- \ll \text{Br}_2$
- ◆  $\text{IO}_4^- < \text{IO}_3^- < \text{I}_2$
- ◆  $\text{ClO}_4^- < \text{BrO}_4^- < \text{IO}_4^-$
- ◆ Rate Limiting Step : Cl - O bond scissoring
- ◆ Kinetically Stable, Thermodynamically Favorable

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## Production of Perchlorate

- ◆ Industrially: electrolysis of aqueous sodium chlorate to form sodium perchlorate
- ◆ All other perchlorate salts and perchloric acid are made from  $\text{NaClO}_4^-$ .
- ◆  $\text{NH}_4\text{ClO}_4$  is produced by an exchange process:
  - ◆  $\text{NaClO}_4^- (\text{aq}) + \text{NH}_4\text{Cl} (\text{aq}) \rightarrow \text{NaCl} (\text{aq}) + \text{NH}_4\text{ClO}_4 (\text{s})$
- ◆ At 200°C,  $\text{NH}_4\text{ClO}_4$  bursts into flame
  - ◆  $2 \text{NH}_4\text{ClO}_4 (\text{s}) \rightarrow \text{N}_2 (\text{g}) + \text{Cl}_2 (\text{g}) + 2 \text{O}_2 (\text{g}) + 4 \text{H}_2\text{O} (\text{g})$

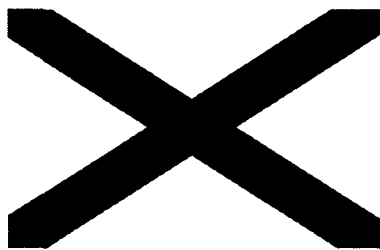
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## Analytical Techniques for Perchlorate Analysis

- ◆ **(In Aqueous Solution)**
- ◆ Liquid-Liquid Extraction
  - ◆ Nitron, Methylene Blue, Brilliant Green, Others
- ◆ Gravimetric Analysis
- ◆ Flame Atomic Absorption Spectrometry
- ◆ UV-Spectrometry
- ◆ Ion Pair High Performance Liquid Chromatography
- ◆ Ion Chromatography

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## Ion Chromatography



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## Perchlorate - Ion Chromatography Methods

- ◆ Pre-Jan 1997- Aerojet Method
  - ◆ MDL = 100 ppb
  - ◆ AS-9 column, NaOH in MeOH/H<sub>2</sub>O, sulfuric acid
  - ◆ 35  $\mu$ L injection volume
- ◆ April 1997 to January 1998 AS-5 Method
  - ◆ California Department of Health Services
    - ◆ Modified Dionex method
    - ◆ Large injection loop volume (740  $\mu$ L)
    - ◆ p-cyanophenol, 120 mM NaOH
    - ◆ AMMS suppression, 35 mM sulfuric acid regenerant
    - ◆ Conductivity detector
    - ◆ MDL = 0.7  $\mu$ g/L
    - ◆ MRL = 4 ppb

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## Perchlorate- IC Methods (Cont'd)

- ◆ April 1998 - Dionex AS-11
  - ◆ Published in AEL, April 1998
  - ◆ Separation on AS-11 anion exchange column
  - ◆ Large injection loop volume (1000  $\mu$ L)
  - ◆ 100 mM NaOH, without modifier
  - ◆ ASRS auto suppression in external water mode
  - ◆ Conductivity detector
  - ◆ MDL = 4 ppb
  - ◆ 2 mM p-cyanophenol, 120 mM NaOH
  - ◆ AMMS suppression, 35 mM sulfuric acid regenerant
  - ◆ Conductivity detector

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## Intra-Laboratory Performance of AS-5 and AS-11

◆	AS-5 *	AS-11 **
◆ MDL ***	1 ug/L	0.25 ug/L
◆ MRL	4 ug/L	1 ug/L
Linear Range	2 - 100 ug/L	2 - 100 ug/L
◆ Spike Recovery	87-98 %	98-99 %
◆ Dup. Analysis	+/- 10%	+/- 10%

- ◆ \* Okamoto, H. et. al. California Department of Health Services, Standard Operation Procedures: Determination of Perchlorate by Ion Chromatography, 3 Jun 1997
- ◆ \*\* Jackson, P. et. al. American Environmental Laboratory, April 1998.
- ◆ \*\*\*Code of Federal Regulations 40, Chapter 1, Pt. 136, Appendix B

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## Effect of pH on IC Response and Stability of $\text{ClO}_4^-$

- ◆ Examine the Stability of  $\text{ClO}_4^-$  with respect to pH
- ◆ Examine the Effect of pH on
  - ◆ Detector Response
  - ◆ Perchlorate Retention Time

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## Stability Study - pH \*

- ◆ Parameters
  - ◆ Perchlorate Concentration: 50 and 100 ppb
  - ◆ pH Levels: pH 5 and pH 9
  - ◆ Storage Conditions: 4°C and Room Temp.
  - ◆ Weekly Concentration Determination
  - ◆ Four Week Duration
- ◆ Method - AS-11 Modified
  - ◆ DX - 500 with Conductivity Detector
  - ◆ 58 mM NaOH in Deionized Water
  - ◆ 1 mL Sample Loop Volume

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◆ \* Contributors: Dickson, S. and Chaudhuri, S., UDOH/DELS

## Stability Study - pH

◆					Standard	
◆ pH	ppb.	Temp.	Mean	Deviation	%CV	
◆ 9	100	cold	98.5	4.2	4%	
◆ 9	100	r.t.	99.7	2.9	3%	
◆ 5	100	cold	97.5	4.6	5%	
◆ 5	100	r.t.	98.7	2.6	3%	
◆ 9	50	cold	47.0	1.8	4%	
◆ 9	50	r.t.	48.8	2.5	5%	
◆ 5	50	cold.	48.7	2.1	4%	
◆ 5	50	r.t.	48.5	2.6	5%	

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- ◆ Between pH 5 and 9, perchlorate is stable beyond 30 days

## Effects of pH on Response and Retention Time

- ◆ Parameters
  - ◆ 50 ppb Perchlorate Prepared in Reagent Water
  - ◆ pH Range: pH 3.8 to pH 9.9 at 1 pH Interval
  - ◆ pH Range was Limited by Instrumentation
  - ◆ Triplicate Analysis
- ◆ Method - Modified AS-11
  - ◆ DX-500 with Conductivity Detector
  - ◆ 58 mM NaOH in Deionized Water
  - ◆ 1 mL Injection Loop Volume

◆ \* Contributors: Dickson, S. and Chaudhuri, S., UDOH/DELS

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## Effect of pH on Perchlorate Retention Time

◆	Mean	Standard	
◆ pH	(min.)	Deviation	%CV
◆ 3.8	12.2	0.01	0.1%
◆ 4.7	12.2	0.01	0.1%
◆ 6.0	12.2	0.03	0.2%
◆ 7.0	12.3	0.01	0.0%
◆ 8.3	12.3	0.01	0.1%
◆ 8.9	12.3	0.01	0.0%
◆ 9.9	12.3	0.01	0.0%

◆ No Retention Time Shift with Respect to Changing pH

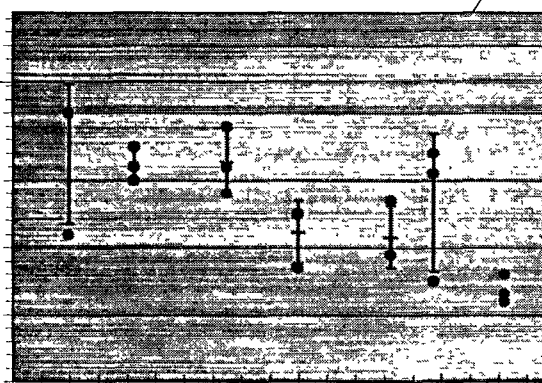
18

# Effect of pH on Ion Chromatography Response

◆ pH	Mean	Std. Dev.	%CV
◆ 3.8	48.4	1.04	2.1
◆ 4.7	48.2	0.25	0.5
◆ 6.0	48.2	0.50	1.0
◆ 7.0	47.2	0.46	1.0
◆ 8.3	47.2	0.43	1.0
◆ 8.9	47.7	1.02	2.1
◆ 9.9	46.4	0.22	0.4

19

# Effect of pH on Ion Chromatography Response



20

## Effect of pH on Ion Chromatography Response

- |  |    |                   |         |               |                 |
|--|----|-------------------|---------|---------------|-----------------|
| ◆ Data Analysis - Linear Regression      |    |                   |         |               |                 |
| ◆ Regression Statistics- Observations 21 |    |                   |         |               |                 |
| ◆ Multiple R                             |    | 0.68850559        |         |               |                 |
| ◆ R Square                               |    | <b>0.47403995</b> |         |               |                 |
| ◆ Adjusted R Square                      |    | 0.44635784        |         |               |                 |
| ◆ Standard Error                         |    | 0.66160414        |         |               |                 |
| ◆  |    |                   |         |               |                 |
| ◆ ANOVA, $N_0$ = No Correlation          |    |                   |         |               |                 |
| ◆  | df | SS                | MS      | F             | Sig. F          |
| ◆ Regression                             | 1  | 7.4957            | 7.4957  | <b>17.124</b> | <b>0.000559</b> |
| ◆ Residual                               | 19 | 8.316681          | 0.43772 |               |                 |
| ◆ Total                                  | 20 | 15.81238          |         |               |                 |

21

## Effects of Methanol on IC Response and Retention Time

- ◆ Parameters
  - ◆ 50 ppb Perchlorate Prepared in Reagent Water
  - ◆ Methanol: 0 to 40%
  - ◆ Triplicate Analysis
- ◆ Method - Modified AS-11
  - ◆ DX-500 with Conductivity Detector
  - ◆ 58 mM NaOH in Deionized Water
  - ◆ 1 mL Injection Loop Volume

◆ \* Contributors: Dickson, S. and Chaudhuri, S., UDOH/DELS

22

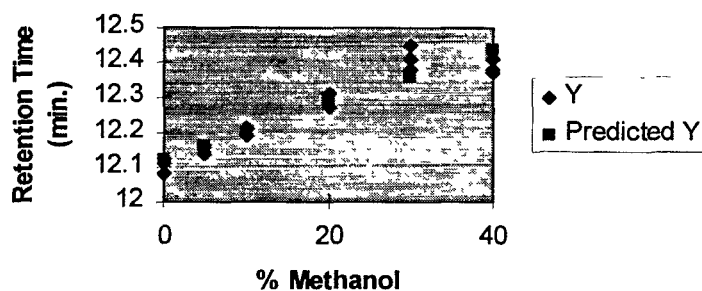
### Effect of Methanol on Perchlorate Retention Time

◆ % Methanol	mean (min.)	std dev	%CV
◆ 0	12.10	0.021	0.2%
◆ 5	12.15	0.012	0.1%
◆ 10	12.20	0.012	0.1%
◆ 20	12.30	0.023	0.2%
◆ 30	12.41	0.035	0.3%
◆ 40	12.40	0.021	0.2%

23

### Effect of pH on Perchlorate Retention Time

Line Fit Plot - %Methanol vs RT



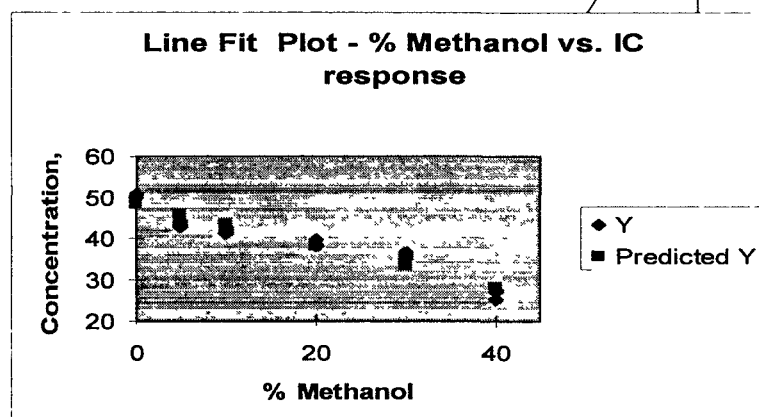
24

## Effect of Methanol on Ion Chromatography Response

◆ % Methanol	mean (min.)	std dev.	%CV
◆ 0	50.50	0.346	0.7%
◆ 5	43.33	0.651	1.5%
◆ 10	41.93	0.702	1.7%
◆ 20	38.83	0.839	2.2%
◆ 30	35.77	0.862	2.4%
◆ 40	26.53	1.159	4.4%

25

## Effect of Methanol on Ion Chromatography Response



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## Collaborative Study on Method Performance

- ◆ Parameters
  - ◆  $[\text{ClO}_4^-]$  Levels: 0, 5.8, 17.9, and 35.4 ppb
  - ◆ TDS Levels: 71, 142, and 284 ppm
  - ◆ Control: 50.8 ppb in Reagent Water
  - ◆ pH: 7.8 to 8.8
  - ◆ Container Types: Plastic and Glass
- ◆ Methods
  - ◆ AS-11 - 13 participants
  - ◆ AS- 5 - 4 participants
  - ◆ Two laboratories elected not to submit results

27

## Results on Method Performance Study (1 of 5)

◆ Sample	C1/T1	C1/T2	C1/T3
◆ $[\text{ClO}_4^-]$ , (ppb)	0.0	0.0	0.0
◆ TDS (ppm)	71	142	284
◆ pH	8.8	8.6	8.5
◆ Mean (ppb)	0.0	0.0	0.0
◆ Std. Dev.	NA	NA	NA
◆ Variance	NA	NA	NA
◆ %C.V.	NA	NA	NA

- ◆ All participants reported "non-detect."

28

### Results on Method Performance Study (2 of 5)

◆ Sample	S/T0 (Positive Control)
◆ [ClO <sub>4</sub> -], (ppb)	50.8
◆ TDS (ppm)	0
◆ pH	7.7
◆ Mean (ppb)	51.79
◆ Standard Deviation	3.77
◆ Variance	14.19
◆ % Coefficient of Variation	7.3
◆ Prepared in reagent water	

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### Results on Method Performance Study (3 of 5)

◆ Sample	C4/T1	C4/T2	C4/T3
◆ [ClO <sub>4</sub> -], (ppb)	35.4	35.4	35.4
◆ TDS (ppm)	71	142	284
◆ pH	8.1	8.4	8.3
◆ Mean (ppb)	35.0	35.5	35.2
◆ Std. Dev.	2.36	2.88	2.80
◆ Variance	5.55	8.28	7.85
◆ % CV	7%	8%	8%

30

### Results on Method Performance Study (4 of 5)

◆ Sample	C3/T1	C3/T2	C3/T3
◆ [ClO <sub>4</sub> <sup>-</sup> ], (ppb)	17.9	17.9	17.9
◆ TDS (ppm)	71	142	284
◆ pH	8.4	8.5	8.5
◆ Mean (ppb)	18.0	17.8	17.9
◆ Std Dev.	1.43	1.54	1.59
◆ Variance	2.05	2.36	2.53
◆ % CV	8%	9%	9%

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### Results on Method Performance Study (5 of 5)

◆ Sample	C2/T1	C2/T2	C2/T3
◆ [ClO <sub>4</sub> <sup>-</sup> ], (ppb)	5.8	5.8	5.8
◆ TDS (ppm)	71	142	284
◆ pH	8.0	8.0	8.0
◆ Mean (ppb)	5.7	5.7	6.0
◆ Std. Dev.	0.74	0.79	1.75
◆ Variance	0.55	0.62	3.05
◆ %CV	13%	14%	<b>29%</b>

- ◆ At low perchlorate concentrations, %CV increases with increasing amount of total dissolved solids

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## Stability of Collaborative Study Samples

- ◆ Collaborative study samples in glass and plastic containers were stable up to eight weeks

33

## Anion Interference Study - AS-11

- ◆ 20 ppb  $\text{ClO}_4^-$  spiked with 100 ppb of each anion

- |               |               |               |
|---------------|---------------|---------------|
| ◆ Arsenate    | ◆ Arsenite    | ◆ Bromate     |
| ◆ Bromide     | ◆ Carbonate   | ◆ Chlorate    |
| ◆ Chloride    | ◆ Chromate    | ◆ Cyanide     |
| ◆ Humic Acid  | ◆ Iodate      | ◆ Iodide      |
| ◆ Molybdate   | ◆ Nitrate     | ◆ Nitrite     |
| ◆ o-Phosphate | ◆ o-Phthalate | ◆ Selenate    |
| ◆ Sulfate     | ◆ Sulfite     | ◆ Thiocyanate |
| ◆ Thiosulfate |               |               |

34

- ◆ Jackson, P. *et al* / Perchlorate Interference Study on AS-11 column

## Anion Interference Studies - AS-11

### ◆ Method

- ◆ Dionex DX-500
- ◆ CD-20 Conductivity Detector
- ◆ GP-40 Gradient Pump
- ◆ AS40 Autosampler
- ◆ 1 mL Injection Loop Volume
- ◆ AS-11 (250 x 4.0), AG-11 (50 x 4.0 mm)
- ◆ Eluent: 100 mM NaOH
- ◆ Flow Rate: 1.0 mL/min

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## Anion Interference Studies - AS-11

◆ Anion	Conc. ClO <sub>4</sub> - (ppm)	Rec. (%)	◆ Anion	Conc. ClO <sub>4</sub> - (ppm)	Rec. (%)
◆ Carbonate	50	96.6	◆ Sulfate	50	94.4
◆ Carbonate	200	98.8	◆ Sulfate	200	100
◆ Carbonate	600	92.1	◆ Sulfate	600	93.4
◆ Carbonate	1000	94.2	◆ Sulfate	1000	97.4
◆ Chloride	50	92.2			
◆ Chloride	200	99.2			
◆ Chloride	60	98.7			
◆ Chloride	1000	97.4			

36

### Anion Interference Studies - AS-11

- ◆  $\text{ClO}_4^-$  retention time (9.0 min.) was unaffected by anions of interest
- ◆  $\text{ClO}_4^-$  does not co-elute with anions of interest
- ◆ Only cyanide (4.38 min.), iodide (4.38 min.), and thiocyanate (6.27 min.) showed significant retention
- ◆ ppm levels of carbonate, chloride, and sulfate have no effect on perchlorate recovery

37

### Anion Interference Studies - AS-11

- ◆  $\text{ClO}_4^-$  retention time (9.0 min.) was unaffected by anions of interest
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38

## Acknowledgement

- ◆ Advanced Technology Laboratories
- ◆ AFRL/Operational Toxicology Branch
- ◆ American Pacific Corporation
- ◆ Applied Research Associates, Inc.
- ◆ Clayton Laboratory Services
- ◆ Dionex Applications Lab
- ◆ Metropolitan Water District of Southern California
- ◆ Montgomery Watson Laboratories
- ◆ Orange County Water District
- ◆ Science and Engineering

39

## Acknowledgement

- ◆ Southern Nevada Water System
- ◆ Thiokol
- ◆ Utah Department of Health - Division of  
Epidemiology and Lab Services
- ◆ Weck Laboratories
- ◆ Clinical Laboratory of San Bernardino San  
Bernardino, CA
- ◆ Edward S. Babcock & Sons, Inc. Riverside, CA
- ◆ State of California Department of Health Services
- ◆ Sanitation & Radiation Laboratories North  
Berkeley, CA

40

## Acknowledgement

- ◆ Steve Dickson
- ◆ Latha Narayanan
- ◆ Joe Humphrey
- ◆ Becky Clewell

41

## Ecological Impact/Transport and Transformation of Perchlorate



Mr. Cornell Long, USAF

Dr. Ron Porter, USAF

Dr. Mark Sprenger, USEPA

Dr. Clarence Callahan, USEPA



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### Introduction

- Background
- Fate and Transport of perchlorate
- Historical Studies
  - Potential ecological receptors
  - Observed Effects
- Proposed Activities and EPA Framework
- Discussion

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### Background

- Perchlorate salts have low volatility, but high solubility
- Solubility leads to high mobility in aqueous systems
  - Surface water
  - Groundwater
- Mobility and persistence may pose a threat to ecological receptors

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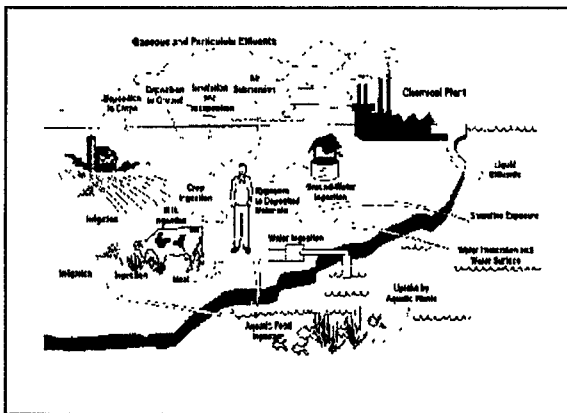
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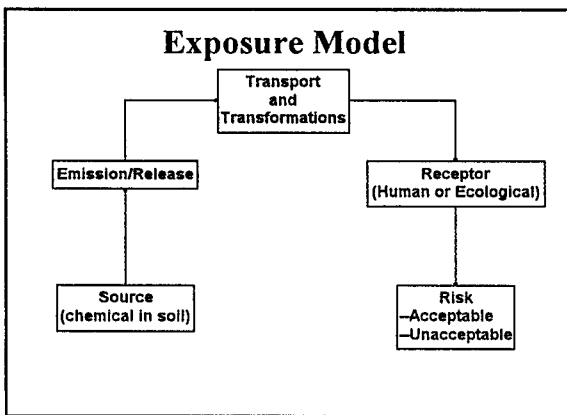
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### Fate and Transport (Transport and Transformation)

- What happens to perchlorate in the environment?
  - Physical characteristics
  - Attenuation processes
- What are the data gaps?




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### Physical Characteristics

- Vapor Pressure--no values found in literature
  - Volatilization not expected to be predominant pathway
- Density--1.95 g/mL
  - Will sink in water
  - Concentrated solutions also more dense than water

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### Physical Characteristics

- Solubility--20.2 g/100g solution
  - Dissolution expected and perchlorate ion will predominate in solution
  - Potential for potassium salt to precipitate--function of ion concentrations
- Standard potential--reduction for Cl from +7 oxidation state to -1
  - All values positive which indicates the reaction is thermodynamically favored

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### Physical Characteristics

- Standard potential
$$\text{ClO}_4^- + 4\text{H}_2 \longrightarrow 4\text{H}_2\text{O} + \text{Cl}^-$$
  - Little evidence that reaction occurs spontaneously
  - Reduction rate negligible at room temperature
  - Conclusion: Perchlorate is kinetically stable (most stable oxo-compound of chlorine)

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### Mobility of Perchlorate



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### Attenuation Processes

- Dilution
- Precipitation
- Biological or chemical reduction
- Adsorption
- Ion-exchange

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### Attenuation Processes

- Dilution--concentrations expected to be significantly lower away from the source
  - However, function of the inert binder may influence source area concentrations
- Precipitation
  - Potassium less soluble, could lead to subsurface precipitation, long-term source area, near source area, and far source area re-dissolution

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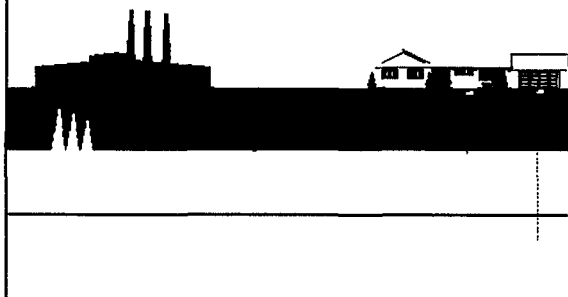
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## Mobility of Perchlorate



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## Attenuation Processes

- Biological or chemical reduction
  - Perchlorate reduction can occur at metal surfaces under acidic pH; however, inhibition by competing anions a problem
- Sorption
  - Perchlorate absorbs weakly to most soil minerals ( $\text{NO}_3^-$  and  $\text{Cl}^-$  more favorable)
  - Minimal impact inhibiting mobility

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## Summary

- Perchlorate is very soluble
- Very stable at low concentrations
- Very inert ion
- Some potential for precipitation in subsurface
- Reduction and sorption occurs to a lesser extent

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### **Data Gaps General**

- Binder Effects
  - Binder chemical degradation rates?
  - Leachability from binder?
  - Concentration of binder + other contaminants?
- Role of reduction and interaction of  $\text{ClO}_4$  with subsurface soils

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### **Data Gaps Site-Specific**

- Soil properties
- Hydrology
- Infiltrating groundwater
- Characterization of leachates produced from source and near source soils

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### **Contact**

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## Historical Studies of Perchlorate Effects

Dr. Ron Porter  
Ecological Toxicologist  
Human Systems Center  
Brooks AFB, TX

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The U.S. EPA Office of Emergency and Remedial Response (OERR), ie Superfund, has adopted a process for designing and conducting ecological risk assessments on chemical stressors at hazardous waste sites.

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The heart of an ecological risk assessment is problem formulation. An effective problem formulation depends upon knowledge of contaminant fate and transport and either mechanism of toxicity and/or sensitive species

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### **We know perchlorates:**

- can affect mammalian and amphibian thyroid functioning
- can affect fish at high water concentrations
- can affect freshwater invertebrates at high water concentrations
- can affect plants

However, mechanism of toxicity is unknown

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### **Outstanding issues for comprehensive problem formulation include:**

- further understanding of environmental fate and transport of perchlorate at low levels in environmental settings
- knowledge of perchlorate bioaccumulation potential and possible sequestering within organisms
- knowledge of possible toxicity mechanisms other than thyroid functioning
- evaluation of exposure mechanisms for ecological receptors

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### **What are potential sources of additional information?**

- Analytical techniques
  - limit the ability to evaluate bioaccumulation
  - limit the ability to evaluate sequestering in organisms
  - limit ability to evaluate exposure
- Use of high exposure toxicity tests

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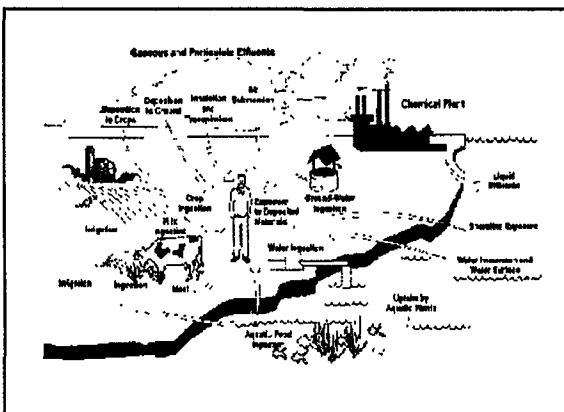
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### In Conclusion:

- The current approach to developing data on the ecological risks from perchlorate have conceptually followed Superfund's ecological risk assessment process.
- Because of the substantial knowledge and analytical limitations which currently exist, careful planning and a diligent problem formulation are critical to the successful evaluation of any potential ecological risk from perchlorate.



### Ecological Receptors

- Aquatic biota
  - Sediment organisms
  - Aquatic plants
  - Aquatic vertebrates (fish)
  - Aquatic invertebrates (clams, crayfish, etc.)

### **Ecological Receptors (cont)**

- Terrestrial biota
  - Soil organisms
  - Terrestrial plants
  - Terrestrial vertebrates (birds, mammals, etc.)
  - Terrestrial invertebrates (insects, spiders, etc.)

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### **Ecological Receptors (cont)**

- Agricultural products
  - Row crops
  - Livestock
  - Commercial fishing
- Food chain concerns
  - Recreational fishing
  - Fruits and nuts
  - Home gardens

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### **Results of Data Search AP Acute Effects-Aquatic**

- Ammonium perchlorate
  - Bacteria            100-1870 ppm (effect)
  - Algae                100 ppm (no effect)
  - Hydra               350-600 ppm (effect)

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**Results of Data Search**  
**AP Acute Effects-Terrestrial**

- Corn (growth) 1-1000 ppm (effect)
- Cotton (seeds) 55 g/sq.m. (effect)
- Ryegrass (seeds) 55 g/sq.m. (effect)
- Soybean (growth) 1-1000 ppm (effect)
- Wheat
  - seeds 0.1-1000 ppm (effect)
  - growth 10 ppm (effect)

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**Data on Other Perchlorates**

- Potassium perchlorate
  - Algae 79-360 ppm (effect)
  - Protozoan 23-1117 ppm (effect)
  - Daphnia 82-670 ppm (effect)
- Sodium perchlorate
  - Fish 3000-7000 ppm (effect)
  - Soybean 2.5-30 ppm (effect)

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**Data on Other Perchlorates**  
**(cont)**

- Nitronium perchlorate
  - Fish 100-200 ppm (no effect)
  - Squash, peanut, corn 1000 ppm (no effect)

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### Results of Data Search

#### Chronic Effects

- No data for effects of ammonium perchlorate on terrestrial or aquatic plants and animals were found in the literature.
- Limited data for effects of potassium perchlorate were found in the literature
  - Two studies on the thyroid of lampreys
  - One study on growth and productivity of soybeans

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### Problem

What appropriate species of animals and plants and what assays are appropriate to evaluate potential ecological effects from exposure to ammonium perchlorate?

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### Proposed Screening Level

#### Bioassays

- |   |                                |
|---|--------------------------------|
| • <i>Daphnia magna</i> or <i>ceriodaphnia dubia</i> | ⇒ Sediment invertebrate        |
| • <i>Chironomus tentans</i>                         | ⇒ Larval sediment invertebrate |
| • <i>Hyallela azteca</i>                            | ⇒ Sediment invertebrate        |
| • <i>Lemna minor</i> (duckweed)                     | ⇒ Vascular plant (aquatic)     |
| • <i>Fathead minnow</i>                             | ⇒ Aquatic invertebrate         |
| • Earthworm   | ⇒ Soil invertebrate            |
| • Microtox  | ⇒ Bacteria (marine)            |

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### Bioassays In Progress


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### Contact

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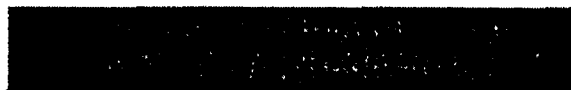
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Interagency Perchlorate Steering Committee



Edward T. Urbansky  
U.S. Environmental Protection Agency  
National Risk Management Research Laboratory  
Water Supply and Water Resources Division  
Cincinnati, Ohio 45268



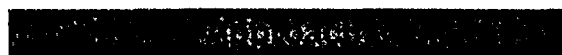
1

Treatment Technologies for Perchlorate Reduction



2

Treatment Technologies for Perchlorate Reduction



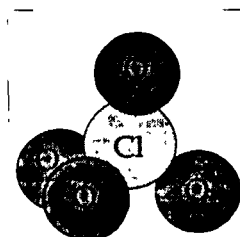
There is no one technique  
that will work for every case.



There is no standard or benchmark  
for evaluating performance.

3

Treatment Technologies for Perchlorate Reduction



1-

- An oxyanion of chlorine
- A strong oxidizing agent (thermodynamics)
- A very sluggish species (kinetics)

4

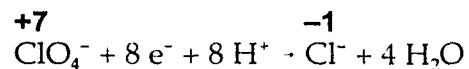
# Treatment Technologies for Perchlorate Reduction

Name	Oxidation State	Formula
Perchlorate	+7	$\text{ClO}_4^-$
Chlorate	+5	$\text{ClO}_3^-$
Chlorite	+3	$\text{ClO}_2^-$
Hypochlorite	+1	$\text{ClO}^-$
Dichlorine	0	$\text{Cl}_2$
Chloride	-1	$\text{Cl}^-$

↑  
Increasing  
oxidizing strength

5

# Treatment Technologies for Perchlorate Reduction

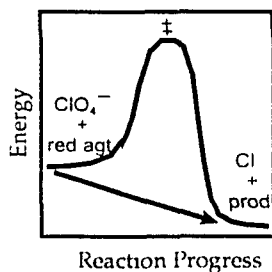


$$E^\circ = 1.287 \text{ volts}$$

A reducing agent transfers electrons to the chlorine atom in a perchlorate ion, converting it to chloride.

6

# Treatment Technologies for Perchlorate Reduction



In general, perchlorate reduction is very slow even though perchlorate is a strong oxidizing agent

Common reductants (e.g., thiosulfate, sulfite) show no measurable reaction

7

# Treatment Technologies for Perchlorate Reduction

A number of air-sensitive metal species can reduce perchlorate, but they cannot be used directly in water treatment because they are still too slow and their products would have to be removed.

Titanium(III)	Methylrhenium dioxide, $\text{CH}_3\text{ReO}_2$
Vanadium(II, III)	Dimolybdenum(III), $\text{Mo}_2^{3+}$
Chromium(II)	Molybdenum(III)
Ruthenium(II)	

8

# Treatment Technologies for Perchlorate Reduction

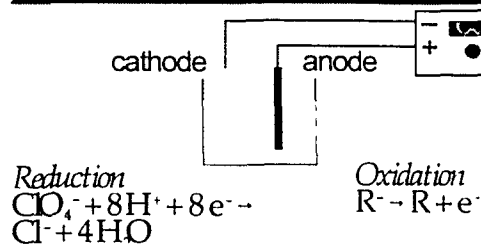
- Expense of materials
- Slowness of reaction
- Toxicity of by-products
- Removal of by-products



9

# Treatment Technologies for Perchlorate Reduction

Electrochemical Reduction of Perchlorate

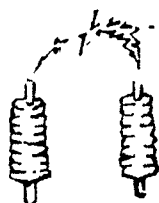


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# Treatment Technologies for Perchlorate Reduction

Electrochemical Reduction of Perchlorate

- Tungsten carbide
- Ruthenium
- Platinum
- Aluminum
- Titanium
- Aluminum oxide
- Carbon (doped with  $\text{Al}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$ )



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# Treatment Technologies for Perchlorate Reduction

Electrochemical Reduction of Perchlorate

- Advantages
  - Nontoxic by-products
  - Well-known technique
- Disadvantages
  - Construction/implementation expense
  - Operation expense (electricity)
  - Electrolysis of water
  - Slowness (reaction and diffusion)
  - Safety (high voltage)

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The use of biological organisms, especially bacteria, to chemically reduce perchlorate to other chemical species

Perchlorate-reducing bacteria



*Ideonella dechloratans*

*Proteobacteria*

*Vibrio dechloraticans* Cuzenove B-1168

*Wolinella succinogenes* HAP-1



USAF, Tyndall AFB, Florida

The bacterium *Wolinella succinogenes* is capable of using perchlorate as an oxidizing agent (electron acceptor) for metabolism.



The USAF and AF Research Labs have developed a bioreactor for this purpose.

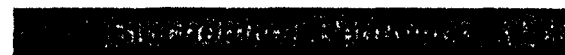


■ Advantages

- Nontoxic by-products
- Versatility
- Speed

■ Disadvantages

- Acceptance
- Regulatory barriers
- Construction/implementation costs
- Hardiness of bacteria



- Bacteria use a biological catalyst or enzyme, called a *reductase*, to reduce perchlorate.
- It may be possible to purify this enzyme and use it directly as a reactant for chemical reduction (addition or tethering)
- Perchlorate reductases evolved from nitrate reductases used by nitrogen-fixing bacteria (e.g., those in legumes).

# Treatment Technologies for Perchlorate Reduction

## ■ Advantages

- ▶ No toxic perchlorate by-products
- ▶ Fast reaction time
- ▶ High effectiveness

## ■ Disadvantages

- ▶ High expense in producing enzyme
- ▶ High maintenance
- ▶ Difficult implementation
- ▶ Enzyme by-products unstudied



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# Treatment Technologies for Perchlorate Reduction

## ■ Anion exchange

## ■ Membrane processes

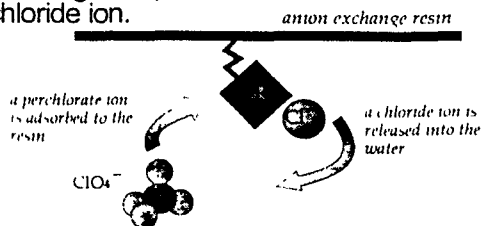
- ▶ Nanofiltration
- ▶ Reverse osmosis
- ▶ Electrodialysis



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# Treatment Technologies for Perchlorate Reduction

A positively charged resin is used to exchange the perchlorate ion for a harmless chloride ion.



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# Treatment Technologies for Perchlorate Reduction

Oak Ridge National Laboratory  
Oak Ridge, Tennessee



Selective pertechnetate ( $TcO_4^-$ )  
removal to parts per trillion  
(pg mL<sup>-1</sup>) levels

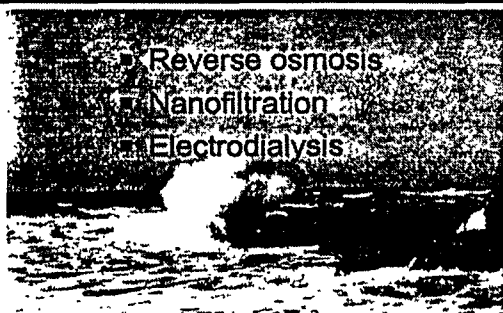
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Anion exchange is used to remove nitrate from water.

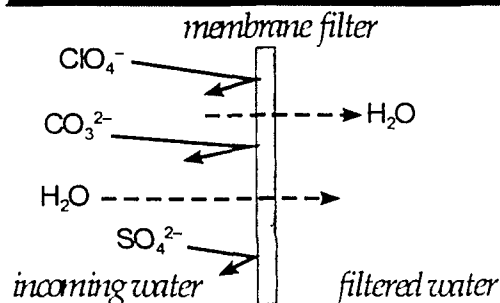


- Nitrate-selective resins already exist.
- Perchlorate and nitrate have similar physical properties (charge, size, aquation).
- Therefore, these resins are expected to be effective in removing perchlorate.
- However, permissible nitrate concentrations are much higher than the perchlorate action level.

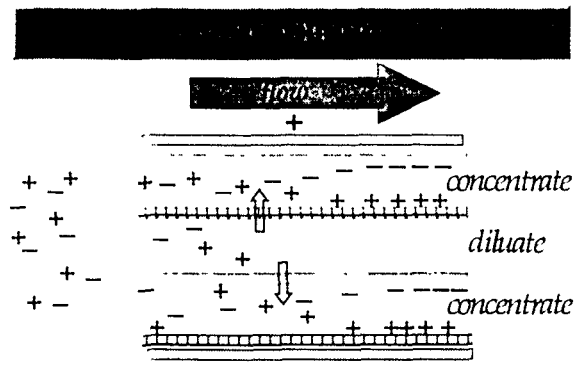
- Advantages
  - Reasonable operating costs
  - Well-developed technique
  - Easy implementation
  - Effectiveness
- Disadvantages
  - Waste disposal from regeneration
  - Moderate selectivity
    - Distribution system effects
    - Resin lifetime



- Reverse osmosis
- Nanofiltration
- Electrodialysis



# Treatment Technologies for Perchlorate Reduction



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# Treatment Technologies for Perchlorate Reduction



- Advantages
  - High effectiveness
  - Low operating cost
  - High throughput
  - Easy implementation

- Disadvantages
  - Low selectivity
    - Distribution system effects
    - Palatability
  - Waste effluent disposal



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# Treatment Technologies for Perchlorate Reduction



- Reverse Osmosis and Nanofiltration
- Ozone/GAC (Chemical Reduction?)
- Biological Reduction
- Anion Exchange

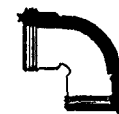


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# Treatment Technologies for Perchlorate Reduction



- Incomplete health effects studies
- Success at reaching trace concentrations
- Distribution system effects



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# Treatment Technologies for Perchlorate Reduction



- Effects on other treatment processes
- Effects from other treatment processes
- Reliability

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# Treatment Technologies for Perchlorate Reduction



- Palatability
- Time
- Expense



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# Treatment Technologies for Perchlorate Reduction



The best solution for a specific situation is likely to be a combination of technologies.

- Anion exchange + bioremediation
- Nanofiltration + blending

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# Treatment Technologies for Perchlorate Reduction

Small systems may benefit from a number of techniques that will not work in large systems.

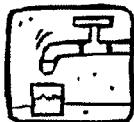
- Reverse osmosis
- Anion exchange



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#### Treatment Technologies for Perchlorate Reduction

- Some techniques lend themselves to point-of-use devices.
- Both anion exchange and RO may be used at individual sites or for very small systems.
- No standards presently exist for purification systems; however, that could be rectified fairly quickly.



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#### Treatment Technologies for Perchlorate Reduction



Congress has appropriated \$2 million to the East Valley Water District for studies on perchlorate.

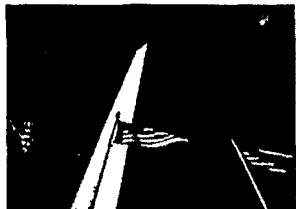
The American Water Works Association Research Foundation has requested proposals.

EPA anticipates an initiative in fiscal year 2000.

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#### Treatment Technologies for Perchlorate Reduction

- Perchlorate is unlike other contaminants already regulated.
- Effective management will require long and short term responses.
- The best solutions will only come about through continued cooperation among state, local, and federal agencies.



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#### Treatment Technologies for Perchlorate Reduction

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**James A. Hurley, Chemical Engineer**

**United States Air Force**

**Tyndall Air Force Base, Florida**

Bachelor of Science degree in Chemical Engineering and Petroleum Refining from Colorado School of Mines, 1982.

Research chemical engineer, from 1982 to 1993, for the National Institute of Standards and Technology. Key programs include: investigation of high-pressure combustion characteristics of selected alloys of construction for the Space Shuttle Main Engine; development of novel reactor systems for chemical generation (excited-state oxygen,  $O_2^1\Delta$ ) and for treatment of hazardous wastes (supercritical water oxidation, oxidation-reduction).

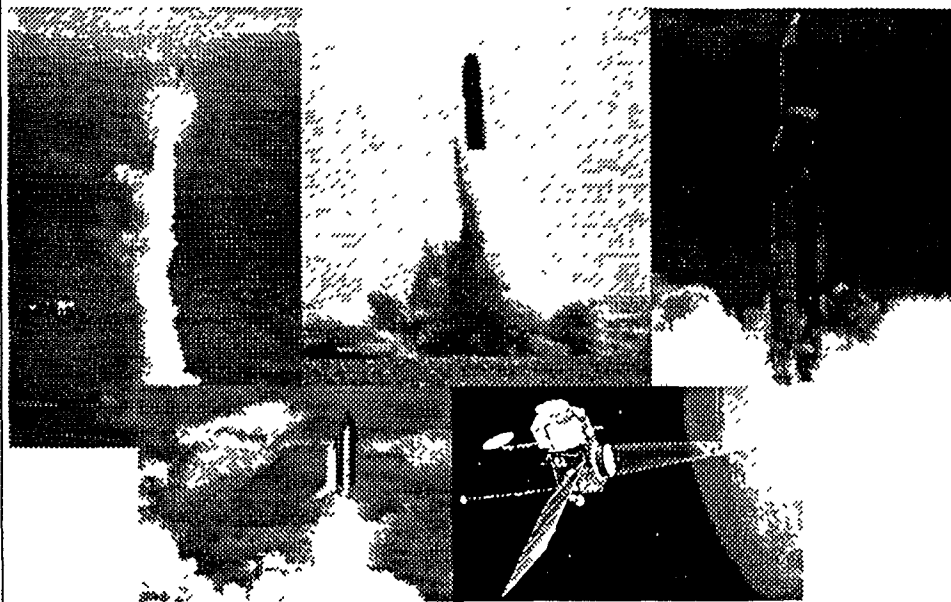
Technical Area Manager, from 1993 to present, developing chemical treatment technology for Air Force Research Laboratory, Materials and Manufacturing Directorate. Key programs include: Large Rocket Motor Demilitarization; Ammonium Perchlorate Treatment Technology, Air Force Industrial Waste Treatment, and Process Simulation and Chemical Systems Modeling.

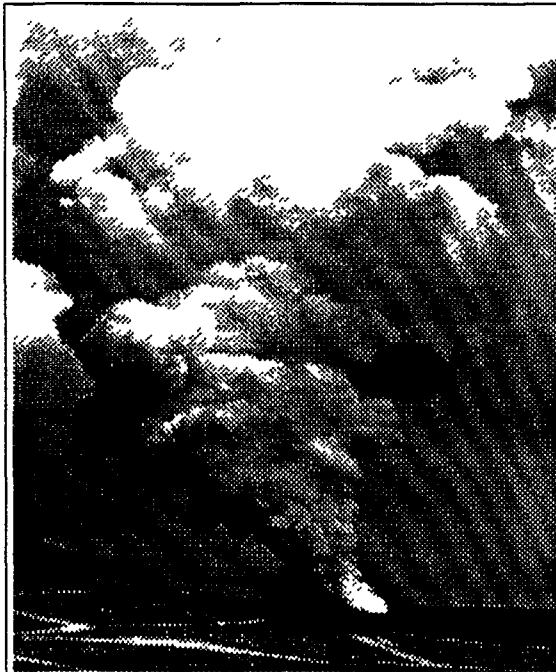
# ***Ammonium Perchlorate Treatment Technology Development***

***James A. Hurley  
AFRL/MLQE  
Tyndall AFB, FL***



***Ammonium Perchlorate - A National Technical Asset  
Integral to Strategic Defense Systems - ICBM, SLBM, NRO***





*Peace Keeper 1st Stage (98,000 lb)*

Requirement

➤ *Increased Demand for Open-Burn/  
Open-Detonation (OB/OD) Facilities  
with Large-Rocket Motor Capacity.*

- *START II*
- *Nunn-Lugar*
- *Non-Proliferation Treaty*
- *Multi-National Force Reduction Treaty*

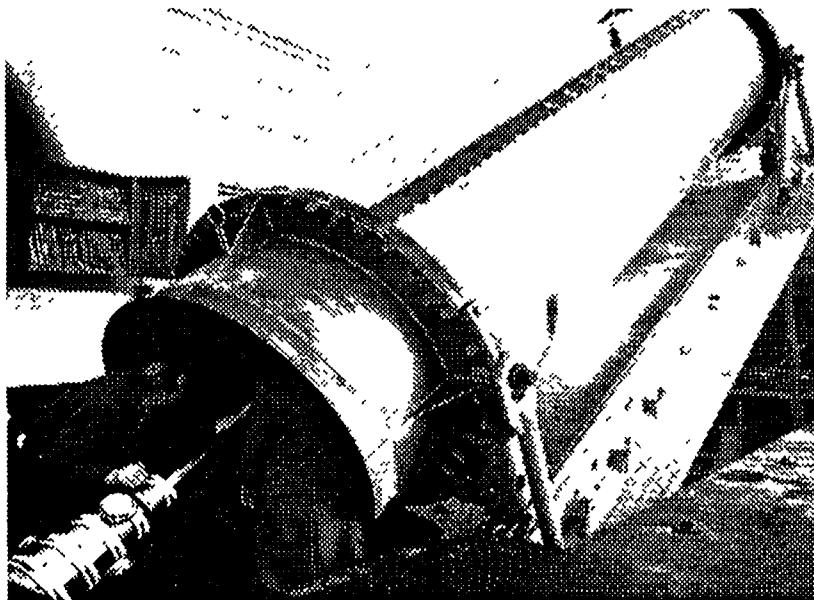
➤ *Decreased Availability of OB/OD  
Facilities.*

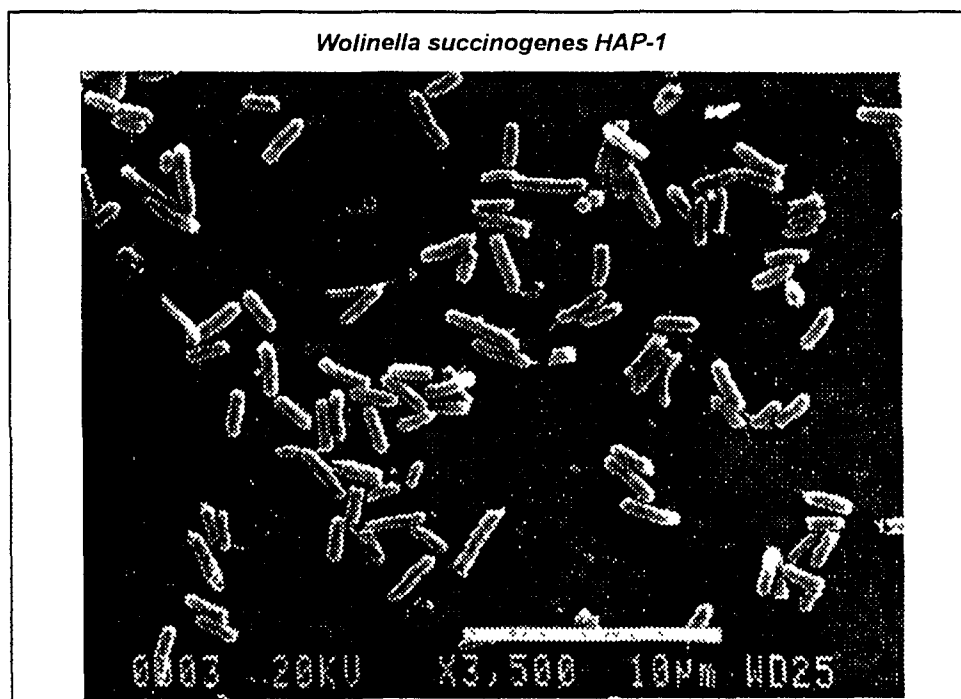
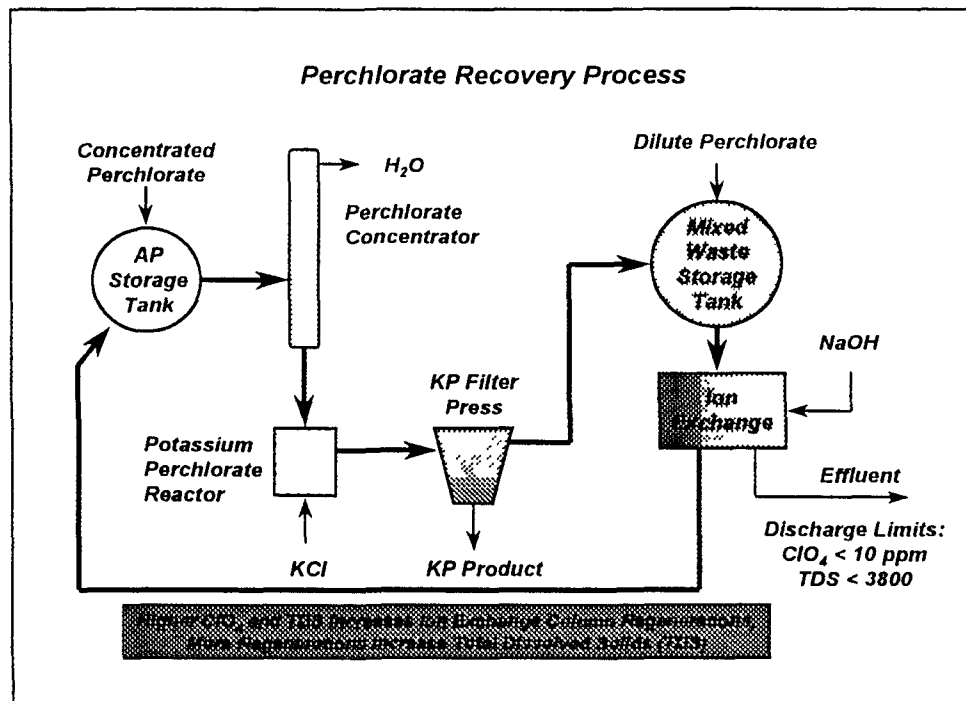
- *Clean Air Act Amendment - 1990 (CAAA)*
- *Base Realignment and Closure (BRAC)*

➤ *Statement of Operational Need  
(SON 003-90)*

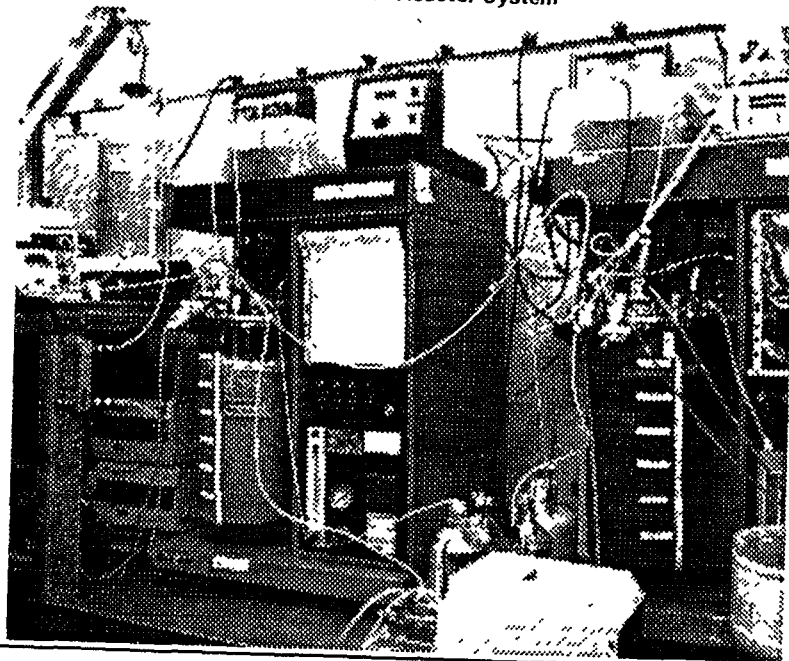
- *Joint Logistics Commanders*
- *Gen McDonald- AFLC/CC*

*High-Pressure Water Washout of Solid Propellant*

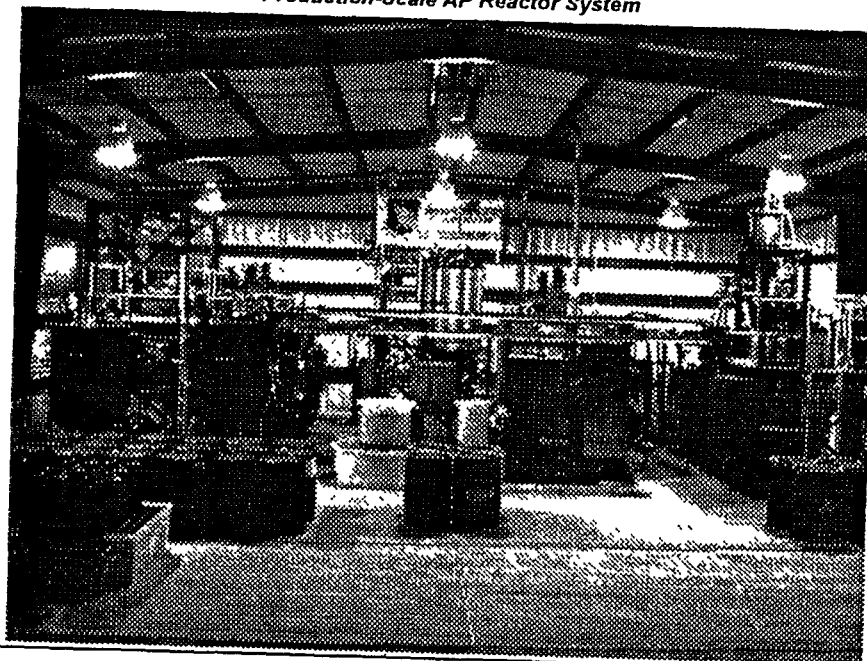




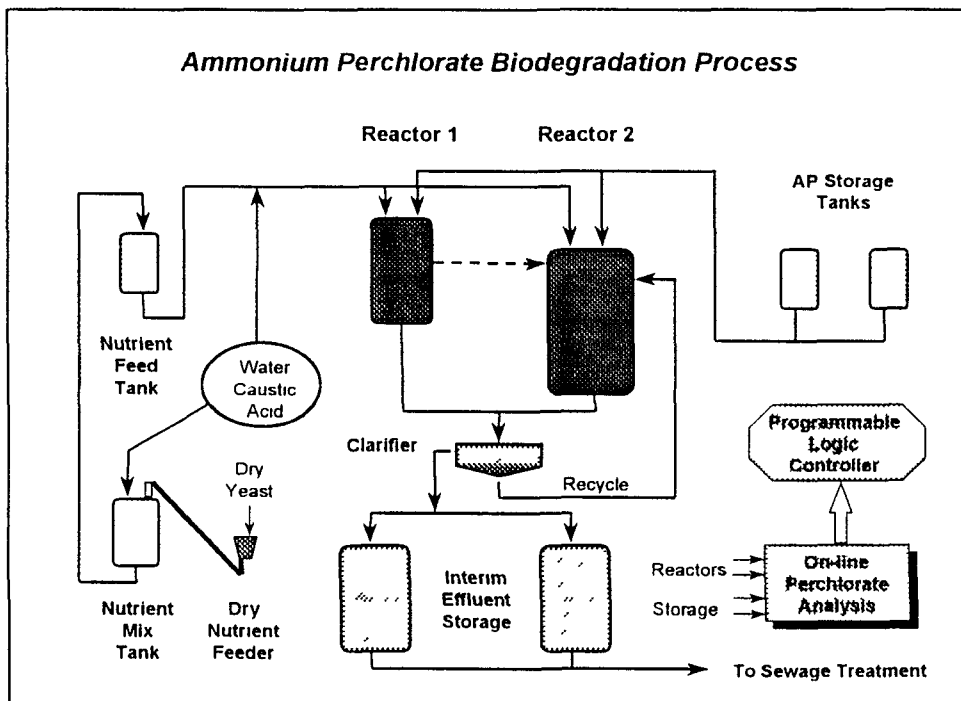
*Bench-Scale Reactor System*



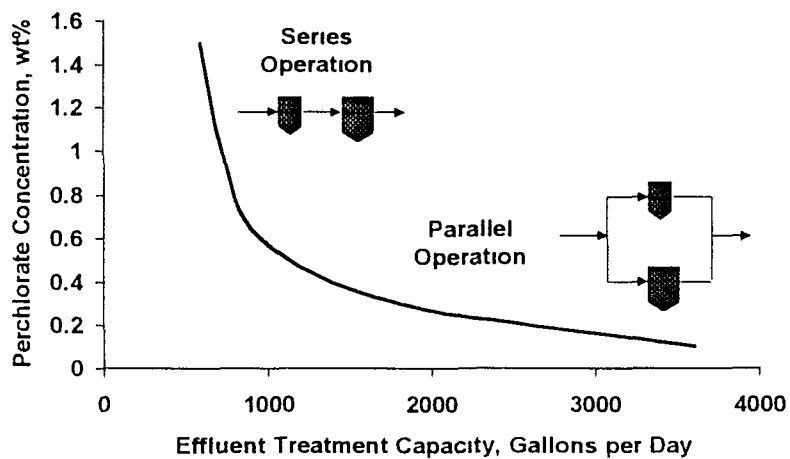
*Production-Scale AP Reactor System*

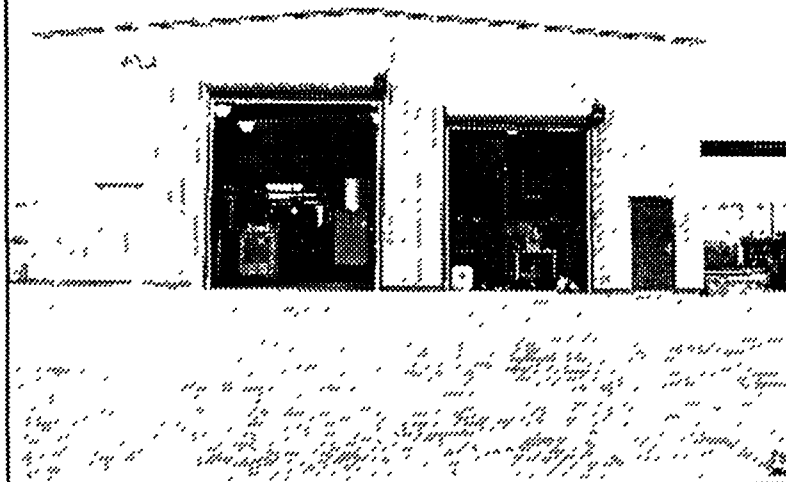


### Ammonium Perchlorate Biodegradation Process

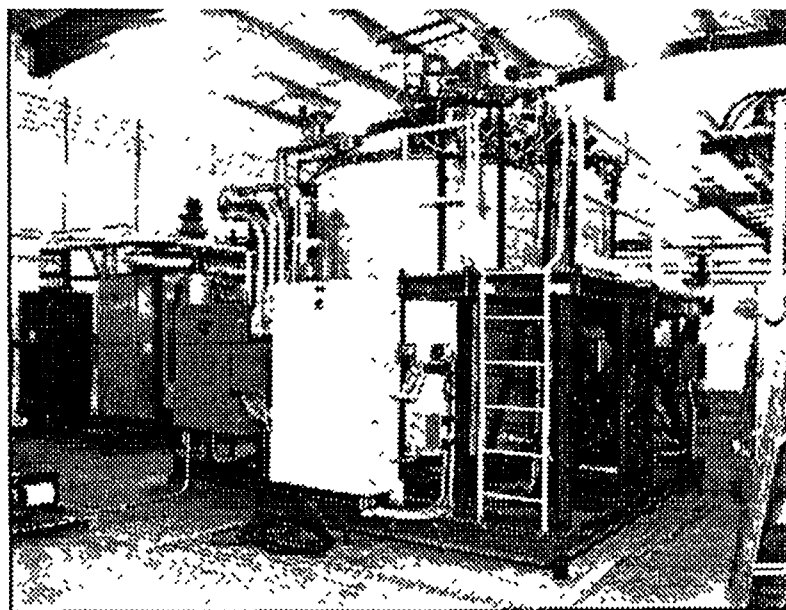


### Effect of Perchlorate Concentration on Capacity



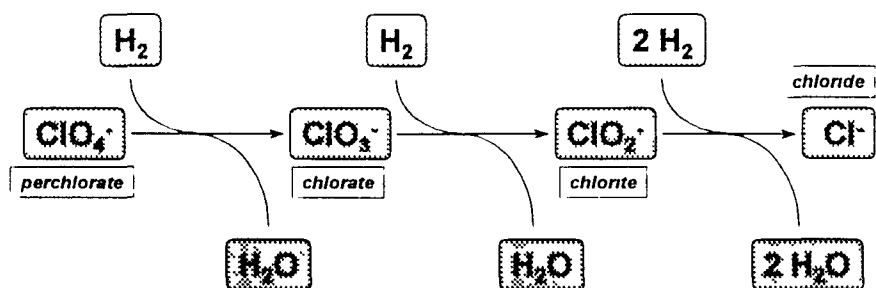


*Building at Thiokol Housing the Ammonium Perchlorate Bioreactor System*

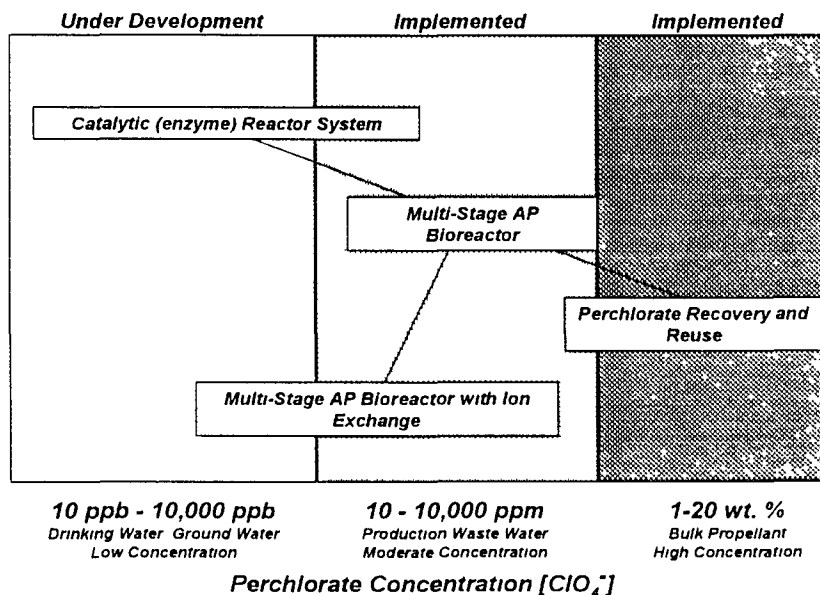


*Primary and Secondary Ammonium Perchlorate Reactors*

**Metabolic Pathway for Energy Production in  
*Wolinella succinogenes* HAP1**



**AP Treatment Technology vs Process Requirement**



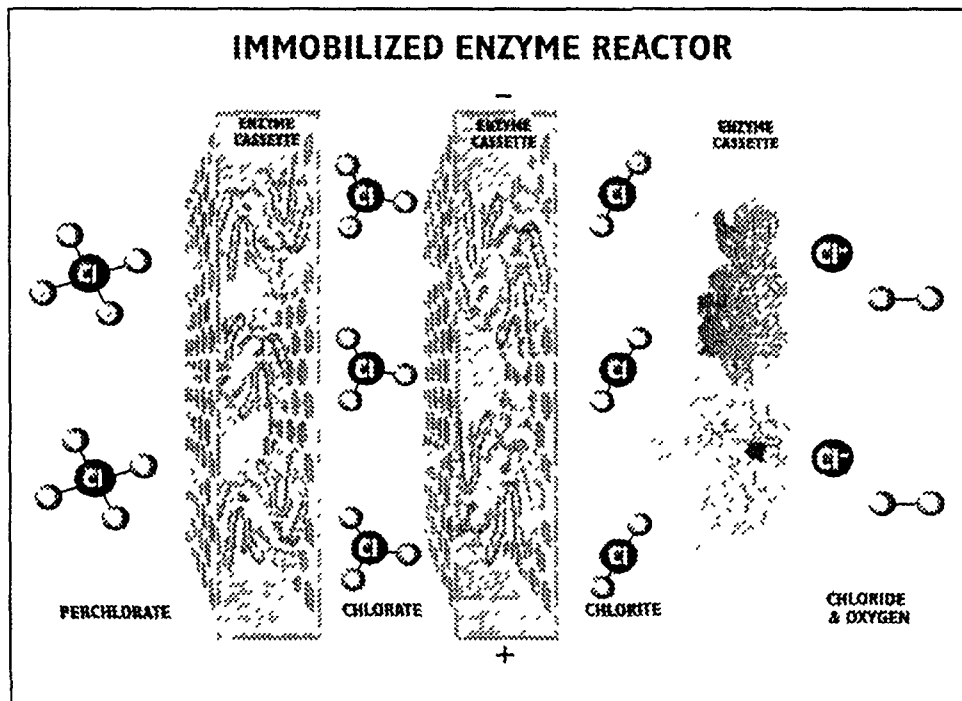
***Low-Concentration AP, High-Volume  
Wastewater Treatment***

**Two Approaches**

- ❶ ***New (or Improved) Unit Operations Enabling Utilization of Demonstrated Moderate-Concentration AP Water Treatment***
  - ♦ ***Reverse Osmosis***
    - *Limited Capacity*
    - *Requires Effluent Reconditioning*
  - ♦ ***Capacitive Deionization***
    - *Small Electrochemical Driving Force Limits Capacity*
    - *Requires Effluent Reconditioning*
  - ♦ ***Ion Exchange***
    - *Resin Regeneration Very Difficult*
    - *Efficacy Uncertain at ppb Concentration Level*
    - *Selectivity Difficult*
    - *May Require Effluent Reconditioning*

***Low-Concentration AP, High-Volume  
Wastewater Treatment (cont.)***

- ❷ ***New Process for Treating Low-Concentration AP Water Directly***
  - ♦ ***Conventional Catalytic Reactor System***
    - *Non-Selective*
    - *Mass-Transfer Limited*
    - *Unknown Kinetics, Unknown Efficacy*
  - ♦ ***Enzyme Catalytic Reactor System***
    - *Anion Specific Selectivity*
    - *High Capacity*
    - *Wide Application Range*
    - *Affect of Other Contaminants Unknown*
    - *Requires Multi-Disciplinary Effort*
    - *System Sustainability Uncertain*



### ***Air Force Benefit***

- *The payoff to the Air Force from this continued effort is reduction of weapon system operational cost as well as ensured continued sustainability.*
- *Manufacturing and maintenance facilities are under ever increasing constraints regarding the life-cycle management of materials used in weapon systems and their manufacture.*
- *Technology insertion opportunities are made possible by the continued participation of MLQ in Air Force unique materials selection, development, and management through the weapon system life-cycle.*

## ***Points-of-Contact***

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